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A

SYSTEM

OF

CHEMISTRY.

A

SYSTEM

OF

CHEMISTRY.

IN FOUR VOLUMES.

BY

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PART II.

A

SYSTEM

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PART II.

OF THE CHEMICAL PROPERTIES AND COMBINATIONS OF INDIVIDUAL SUBSTANCES.

IN proceeding to this department of the science, it is necessary to explain the principles on which its arrangements are founded.

The relations in the chemical constitution and properties of bodies, whence their classification as objects of chemistry must be derived, are so various, and admit of being surveyed under such different aspects, that numerous systems of arrangement, all of them to a certain extent just, may be, and have been framed.

Two general methods, admitting indeed of considerable diversity in the details, appear to be suggested by the nature of the science itself. Its leading object is to investigate the combinations of matter, to resolve bodies therefore into their constituent principles, and ultimately into their first elements; and at the same time to determine all the combinations into which these principles are capable of entering.

When a certain number of simple or elementary bodies are thus discovered, these may form the basis of a chemical classification : they may be associated in orders according to their chemical agencies ; and the compounds they form may be arranged according to a series of analogous combinations, in relation to the elements of which they are composed.

Another method the reverse of this may likewise be adopted. Substances may be classed according to analogies in their chemical properties, independent of their chemical constitution : their composition may be investigated, so as to discover their elements, and these may be connected with the compounds from which they are obtained.

The former of these gives a synthetic, the latter an analytic classification.

Had Chemistry attained the ultimate objects of its researches, had the elements of matter been discovered, and all their combinations traced, a synthetic classification would exhibit the real relations of the science, and in this respect would form a perfect system. But its actual state is very remote from this. The substances considered as simple are so only with regard to our knowledge of them ; the uniform result of chemical investigation has been to establish as compounds, substances, the composition of which had been unknown ; and we have no proof that we have obtained in an insulated state any body truly elementary. No synthetic chemical arrangement, therefore, which can at present be framed, can with any probability be considered as stable : and, at any period, such arrangements are always to a certain extent imperfect from the progressive state of the science. Substances not decomposed must often be assumed to be compound, from their intimate connection with others, the composition of which has been effected ; or, if this is avoided, and the principle of the arrangement rigidly adhered to, the most obvious analogies must often be violated, and the classification be

rendered altogether discordant.   They farther lead to much subdivision in following the series of combinations, and in general to a very artificial order; and they are liable to the important objection, that considered as designed to convey a knowledge of chemistry, they impose the difficulty of substances being presented to the attention of the student with which he is not familiar, to the knowledge of which he is not led by any previous acquisition, and which in many cases are arrived at, only by complicated processes of investigation,—a difficulty which must become greater as the science advances; for in proportion to the extent to which analysis is carried, the ultimate principles must be more remote from the natural bodies at which the analysis has commenced.

These considerations induced me, a number of years ago, to relinquish the synthetic plan of arrangement which I had formerly adopted, and to which chemists have generally shewn a preference, and to adopt an analytic system; —to take substances as they are presented by nature, connect them by relations in chemical properties, and thus form them into classes independent of their constitution; and with those which are compound to associate their elements so far as these have been discovered.   Such arrangements exhibit the science in its simplest form, and facilitate its acquisition by presenting its facts in the most natural order : they are little liable to be subverted by the progress of discovery, since they easily assimilate with it : the classes being established on relations in properties, rather than in composition, are more permanent ; and there is no necessity for aiding the classification by assumptions from analogy, which, on the opposite principle, the imperfect state of knowledge so often demands.   I have accordingly had every reason to be satisfied with the arrangement I proposed.

In the present edition I have adopted one important modification of it, in consequence of some views of chemi-

cal theory which have recently occurred to me. I had placed the two orders of alkalies and earths before the order of acids. I have been led to reverse this arrangement, and to place the acids first, as the views to which I allude bear a relation more particularly to the constitution of the acids, and admit of being extended to the alkalies and to the earths with more advantage when the doctrine has been previously illustrated and applied to the theory of acidity. But, independent of this, the method now stated has the important advantage of following a more natural order; for it connects directly the fixed alkalies and the earths with the metals. The bases of the former are substances which have unquestionably the greater number of metallic properties : And the transition is unbroken from the alkalies, through the earths to the metallic oxides. It is an advantage in the arrangement, therefore, to establish this connection, and to render the series complete.

Another change has been introduced as the consequence of this. The order of salts has been usually subdivided into genera, according to the acid entering into the composition; and, in particular, the salts which have the alkalies and earths as their bases, have been arranged on this principle. In the preceding edition they were accordingly placed under the respective acids. But this necessarily required that these bases should have first been considered, and, of course, that they should occupy a previous place in the arrangement; and it was this which induced me formerly to follow this plan. The circumstances I have stated having led me to adopt the reverse order, a different mode must be followed with regard to the salts.

There are two methods which admit of being employed. The salts may be placed as a distinct order, which may itself occupy a place in the arrangement succeeding the acids and the bases of which they are composed : Or the salts formed by the combination of each base with the

different acids may be placed in connection with the base itself.

The former of these methods is perhaps more systematic, but it is liable to the great objection of insulating and placing at a distance from each other substances which are intimately connected, and are best considered in connection—of giving the history, for example, of the salts of each metal apart from that of the metal itself, though they form the most important part of its chemical relations; while there is the additional disadvantage, in a work designed in some measure for elementary instruction, of bringing together a number of substances comparatively unimportant and uninteresting. The other method is not liable to these disadvantages, but it is not altogether free from objection. In the metallic salts the genera are best formed in relation to the metal; for its general properties remain in the compounds which it forms with the different acids. But in the salts, of which the alkalies and earths are the bases, it is rather the reverse; the properties are apparently more dependent on the acid than on the base; and hence it is preferable, rather to form them into genera in reference to the former, than to the latter. But although this objection has some weight, it does not appear to me to be such as to lead to a preference of the opposite method. It still remains true, that the metallic salts bear the most obvious relation to their base, not to the acid, and their genera therefore ought to be established from the former, not from the latter. This is true, even to a certain extent, with regard to those of the earths,—to the aluminous for example, and the magnesian salts; and even the salts of one of the alkalies, ammonia, exhibit, in a striking manner, the same relation. Uniformity leads to the adoption of the same method with regard to all. And hence I have not hesitated to adopt the arrangement of placing all the salts under genera in reference to the base of which they are formed.

At the same time, to retain in view the opposite rela-
tion, I have given, under the history of each acid, the ge-
neral chemical properties, and the distinctive characters of
the salts which it forms with the different bases:— under sul-
phuric acid, for example, the characters of the sulphates
as a genus, under the nitric acid those of the nitrates, and
the same with regard to the others, while the individual
salts are placed under the base of each.   In this manner ·
I believe every advantage is attained, and the method is
preferable to the only other that can be adopted,—that of
placing the whole salts as an order, and subdividing this
into genera, either according to the acid or the base.

The following Table presents a view of the Classifica-
tion, including, to render the System complete, the First
Part, which has been the subject of the preceding volume.

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BOOK I.

OF ATMOSPHERIC AIR, AND ITS ELEMENTS.

THE atmosphere, or that mass of elastic fluid which sur-
rounds the globe to a great height, diminishing in density
as it recedes from the surface, may be regarded, under
one point of view, as a collection of all those substances
which are capable of existing at natural temperatures in
the aërial form, and which are disengaged, more or less
abundantly, by the processes carrying on at the surface of
the earth.   These, with other substances which they can
hold in solution, with watery vapour, the effluvia from
animals and vegetables, and with the magnetic and elec-
tric fluids, light and caloric, form a vast mixture, the com-
position of which it is apparently impossible to determine
with accuracy.

Chemical analysis has discovered, however, that in this
mass there exists an elastic fluid of uniform composition,
with which other substances are merely mingled ; these
are never in any large proportion, and are even seldom
discoverable by chemical tests ; they are only occasionally
produced ; and are quickly abstracted by various natural
processes, by which the purity of the atmosphere is pre-
served.

This elastic fluid, which forms the great mass of the in-
ferior portion of the atmosphere, consists principally of
two substances, oxygen and nitrogen, which exist natural-
ly in the gaseous form, and of a very small portion of ano-
ther gas,—carbonic acid.   It has also been supposed, that

as hydrogen gas, more or less pure, is evolved from various natural chemical processes, it may, from its greater levity, accumulate in the higher regions. There seems little reason to believe, however, that elastic fluids separate from each other, and arrange themselves according to their specific gravities ; they rather remain in a state of equal diffusion ; and the composition of the atmosphere is therefore probably at all heights nearly the same.

The composition of atmospheric air is discovered by experiments which present very simple results. When it is submitted to the chemical action of certain substances,— of phosphorus for example, or of the liquor formed by boiling lime and sulphur in water, it suffers a diminution of volume, rather more than one-fifth, and the air which remains has no longer the same properties ; it is in particular incapable of supporting combustion, or of sustaining animal life. These changes are owing to the abstraction of an elastic fluid, oxygen gas as it is named, which in its pure form is eminently capable of supporting combustion, and of enabling animals to live by respiration. The residual air is the nitrogen gas with which the oxygen had been mixed or combined. If there be added to it a portion of oxygen gas equal to what had been abstracted, an air is formed perfectly similar to atmospheric air. Thus, the chemical constitution of the elastic fluid forming the atmosphere is demonstrated both by analysis and synthesis, and we are led to the knowledge of these two aëriform fluids, oxygen and nitrogen gases, as its constituent principles. The history of these being delivered, we may consider with more advantage the chemical constitution and properties of the mixture or compound they form.

CHAP. I.

OF OXYGEN GAS.

THIS important chemical element was discovered nearly about the same time by Priestley and Scheele. In 1774, Priestley obtained it in an experiment in which he exposed red oxide of mercury to the heat of the solar rays concentrated by a lens; and he observed its distinguishing property of rendering combustion vivid. Scheele in 1775 procured it in the distillation of nitrous acid, in the decomposition of nitre by heat, and from a mixture of black oxide of manganese and sulphuric acid, and observed in it the same property. Lavoisier, from experiments on the change which metals suffer when heated in atmospheric air, began to suspect, as he expressed it, that the air of the atmosphere, or an elastic fluid contained in the air, was capable of being fixed and combined with metals. In a memoir read before the Academy of Sciences in 1775, he gave an account of an experiment, in which, by heating in a retort red oxide of mercury, he obtained an air in which he observed inflammable bodies to burn with an enlarged flame, and with more light than in common air. But prior to this he seems to have been acquainted with the discovery by Priestley.

Different names were given to this elastic fluid. Scheele named it Fire Air, partly from its superior power of exciting combustion, and partly from supposing that it entered into the composition of fire. Priestley gave it the name of Dephlogisticated Air, as being air, as he supposed,

free from Phlogiston. Lavoisier called it Air eminently pure; and afterwards, finding that when breathed by animals it supports life longer than any other air, Air eminently respirable. Condorcet imposed the appellation of Vital Air, derived from the same property, and Bergman that of Pure Air. These names are incapable of being employed in the formation of derivative terms. At the framing of the new nomenclature, it was necessary that a name should be invented, having this advantage; and Oxygen, derived from the Greek word ὀξύς, sour or acid, was preferred, it being a distinctive property of this substance to form combinations possessed of acidity. In conformity to the principles of the nomenclature, Oxygen denotes the solid base or gravitating matter, and Oxygen Gas is the name given to it in the aërial form.

Oxygen is a principle extensively diffused. In the state of gas it forms one-fifth part of atmospheric air; it constitutes a principal part of the composition of water; it is an element of acids, and hence is an ingredient in many saline and mineral substances; it also exists in the composition of the alkalis and earths; it is found in nature, combined with many of the metals; and it is a constituent part of the greater number of vegetable and animal products. It is nowhere, however, perfectly pure, and certain processes are requisite to obtain it in this state.

In several of its combinations it is retained by an attraction sufficiently weak to admit of being disengaged by an elevation of temperature. In common nitre it exists in great quantity; and when this salt is exposed to a red heat in a coated glass or earthen retort, oxygen gas is disengaged, mixed, however, with a portion of nitrogen gas. From 1 lb. of nitre about 1200 cubic inches of oxygen gas are obtained. It can be separated by a similar process from some of its metallic compounds. By Priestley it was procured from red lead, and by Lavoisier from red oxide of mercury. The black oxide of manganese, a mineral

substance, affords it with more facility, and in greater quantity, and it is from it that for common experimental purposes oxygen is generally obtained. A quantity of it in powder is put into an iron bottle, to which a metallic tube is adapted, Fig. 49, Plate IV, which terminates in connection with a gazometer or the pneumatic trough. The bottle is put into a furnace or common fire, and when the temperature is raised to a high red heat, oxygen gas is disengaged, is conducted by the tube, and transmitted through the water in the gazometer or in the trough, so as to be collected in the manner already described, vol. i, p. 295.

The expulsion of the oxygen in this operation is owing to the repulsive agency of the heat applied. Manganese is a metal which exists in combination with different proportions of oxygen. In the black oxide it is combined with the largest proportion ; the tendency of the oxygen is to exist in the elastic form ; this is repressed by the attraction exerted between it and the manganese, but the elevated temperature favouring the elasticity of the oxygen counteracts the attraction, and admits of a certain portion of the oxygen escaping in the aërial state. When a certain portion has thus been abstracted, the remaining quantity is retained by a more powerful attraction, conformable to the general law already illustrated, (vol. i, p. 121.) that the attraction which one body exerts to another is more powerful in the first proportions with which it combines, than in larger proportions. Hence the whole of the oxygen is not expelled, but a portion of it still remains combined with the metal at the most intense heat.

The abstraction of the oxygen is much facilitated by the introduction of certain affinities, so that it can be effected by a more moderate heat ; and this method is usually adopted on a small scale. Two parts of black oxide of manganese are mixed with $1\frac{1}{2}$ of sulphuric acid in a glass

retort. On applying the heat of a lamp to the retort, oxygen gas is expelled, and may be received beneath an inverted jar, filled with water, and placed on the shelf of the pneumatic trough : it is mixed with vapour, which renders it opaque, but which is soon absorbed by the water. The agency of the sulphuric acid in facilitating the disengagement of the oxygen gas is explained on the following principle. A metal combines with an acid only when it is previously combined with oxygen. But it is a general law, (to be afterwards illustrated,) that the attraction exerted by the acid is more powerful to the metal in a low degree of oxidation, that is, combined with a small proportion of oxygen, than it is to the metal in a high degree of oxidation, or combined with a larger proportion of oxygen. From the operation of this law, the sulphuric acid favours the expulsion of a portion of the oxygen of the oxide of manganese, at a degree of heat comparatively moderate, and combines with it in a lower state of oxidation. The same result is obtained with red oxide of lead.

When oxygen gas is to be procured in the state of greatest purity for more delicate experimental investigations, the substance employed to afford it is a salt named oxymuriate of potash. One-third of its weight consists of oxygen : this is expelled by a red heat, and the salt contains no other principle which can be disengaged, so as to assume the aërial form ; by rejecting the first portions that pass off, which are necessarily mixed with the atmospheric air of the vessel, the oxygen gas may be collected pure. One grain of the salt yields rather more than a cubic inch of the gas.

Oxygen gas is likewise yielded by growing vegetables exposed to the rays of the sun, and it escapes even in small quantity from the leaves of plants laid on the surface of water, and exposed to solar light.

Oxygen gas is colourless ; it has neither smell nor taste ; is rather heavier than atmospheric air ; its specific gravity,

referred to that of water as 0.1000, is .001356 ; or, refer-
ring it to atmospheric air as 1000, it is, according to Kir-
wan, 1103, to Lavoisier 1102, to Davy 1127, and to Biot
and Azago 1.10359. 100 cubic inches weigh, according to
Davy, at the temperature of 55°, and the barometrical
pressure of 30, 35.06 grains ; according to Allen and Pe-
pys, 33.82 grains at a temperature of 60°, and a pressure
of 30.   The most accurate estimate seems to be that of 34
grains.

This gas is absorbed by water, but in a quantity so in-
considerable that any diminution in its volume from agita-
tion with that fluid is scarcely perceptible.   Dr Henry has
shewn that 100 cubic inches of water, freed from air by
boiling, absorb of oxygen gas exposed to it, for several
hours, and frequently agitated, under a common atmo-
spheric pressure, and at the temperature of 60°, 3.55 cu-
bic inches *.   By increasing the pressure, a larger quan-
tity is absorbed ; and, from the experiments of Paul of
Geneva it appears, that, under a great pressure, water may
be made to take up about half its bulk of the gas, acquir-
ing, however, from this impregnation, no taste or smell.

The most characteristic property of oxygen gas is its
power of exciting and supporting combustion.   When an
inflammable body is kindled and introduced into it, it burns
with increased splendour ; it burns too for a longer time,
a larger quantity is consumed, and more heat and light are
evolved, than when it burns in atmospheric air.   The flame
of a taper is enlarged and becomes dazzlingly bright ; other
combustibles, as sulphur, charcoal, or phosphorus, burn
brilliantly ; and even some which do not suffer combustion,
when raised to a red heat in atmospheric air, as iron, burn
when they are at this temperature immersed in oxygen gas.
Bodies burn indeed in atmospheric air, and in some other
gases, only from the oxygen they contain.   During com-

* Philosophical Transactions, 1808.

bustion, the oxygen combines with the burning body, and the products of combustion are therefore compounds of oxygen.

These compounds have frequently the characteristic properties of the class of substances denominated Acids. From the researches of Lavoisier, it appeared even that oxygen enters as an element into all acids, the composition of which had been determined; hence it was regarded as the principle of acidity, and from this the appellation assigned to it was derived. The proposition that oxygen communicates acidity to the combinations into which it enters, is true to a certain extent; but it does not do so exclusively. There is another element, hydrogen, the action of which is productive of the same result. And the united action of these two bodies, I shall afterwards endeavour to shew, gives rise to a still higher degree of acid power. The same elements, there is reason to believe, produce alkalinity as well as acidity.

Oxygen gas is distinguished by its power of supporting animal life. If an animal be confined in a given quantity of it, it lives for a longer time than it would do in the same volume of atmospheric air. A quantity of oxygen is consumed during respiration; a due supply of it is even indispensable to the continuance of life; and atmospheric air sustains life, only from the oxygen it contains and is capable of affording to the blood. This fluid, when exposed to oxygen, becomes of a florid red; a change of colour which it also suffers in the lungs. The pure gas does not appear, however, to be well adapted to animal existence. If an animal be confined in a quantity of it, its respiration becomes hurried and laborious before the whole of the oxygen is consumed, and it dies even though so much oxygen is still present, that another animal of the same species, introduced into the residual air, will live. It has been concluded from this, that oxygen proves too highly stimulating, and hence the necessity of an atmosphere such

as ours is, in which oxygen is diluted with another air, which appears to be nearly negative in its effects.

Oxygen has a tendency to combination, more extensive perhaps than any other chemical agent has. It is necessary to support combustion, and during that process it combines with the combustible body. The products are consequently compounds of oxygen, and these compounds are numerous and important agents in chemistry. The acids are of this kind, and their activity is principally dependent on their oxygen, which they yield to other bodies, and which, by the dense state in which it exists, is often capable of exerting powerful affinities. All the metals are capable of combining with this principle : And it exists in an immense number of natural substances. There are not many even in which it is not contained. It is therefore more abundant in nature, and more extensively diffused than any simple substance; its affinities are more numerous and more energetic ; the development of its agencies formed the principal part of what has been named the modern theory of chemistry, and they still afford the most important relations of the science.

The peculiarity of oxygen deserves to be remarked as intimately connected with its chemical agencies,—that of all bodies, it is the one having in the highest degree that relation to electricity, in consequence of which it is attracted, when under electrical influence, to the positive electrical pole ; it even impresses this property on the compounds in which it predominates ; and perhaps they alone possess it. Oxygen is also one of those bodies, the combining quantities of which are comparatively small, and which probably therefore approach nearest to the elementary state.

CHAP. II.

OF NITROGEN GAS.

WHEN the oxygen gas of atmospheric air has been abstracted, there remains an elastic fluid equal in volume to nearly four-fifths of the air. This gas has been designated by the appellation of Azote, or of Nitrogen. The former of these terms, derived from α *privative*, and ζωή *life*, implies that it is incapable of sustaining, or that it proves noxious to life; but this property, so far from being peculiar to it, belongs to nearly all the aëriform fluids, and to many of them in a more eminent degree than to this one, and therefore cannot be made the basis of a distinctive name. A principle of the modern nomenclature, too, is, that the names of the compounds which any simple substance forms with oxygen, should be derived from the name of that substance. The combinations of this gas with oxygen have been long known by the epithet Nitrous, one unexceptionable, and which it would therefore have been improper to change; hence the framers of the nomenclature, by adopting Azote as the name of the base, violated unnecessarily the principles by which they professed to be guided. The term Nitrogen, proposed by Chaptal, accords with these principles, and is unexceptionable: the slight variation of Nitron might, however, be preferable, from considerations of analogy. Other appellations have been given to this gas. It was named by Priestley Phlogisticated Air; Foul or corrupted air by Scheele; and Mephitic air by Lavoisier; these have properly fallen into disuse.

Nitrogen gas had been observed to remain after combustion in atmospheric air. But being frequently mixed with aëriform products of that process, and approaching in its properties to another gas, Carbonic Acid, the Fixed Air of the older chemists, its distinctive properties had not been accurately observed, nor its existence as a peculiar substance recognised. The difference in its properties from those of fixed air seems to have been first taken notice of by Dr Rutherford and Dr Priestley, nearly about the same time, 1772. Dr Rutherford, in an inaugural dissertation, remarked, that when from air vitiated by respiration, the fixed air is removed by an alkaline solution, the residual air does not regain its salubrious quality, but extinguishes flame, and destroys life, though it gives no precipitation with lime water. Priestley observed similar results, from air diminished in volume, by having been exposed to the action of iron-filings and sulphur moistened, or submitted to the calcination of metals: And Scheele, who about the same period had made the same observation, concluded that it is a peculiar kind of air, a constituent part of the atmosphere, and not, as had been supposed, atmospheric air vitiated by the processes in which it is obtained. Lavoisier drew the same conclusion, though without pointing out so clearly its distinct existence, or its characteristic properties.

It is from atmospheric air that this gas is generally procured, the air being submitted to the action of substances which abstract its oxygen. The easiest process is to kindle a bit of phosphorus in a jar containing atmospheric air; the proportion of phosphorus being at least half a grain to a cubic inch of air: in the combustion the oxygen is consumed; the residual air is nitrogen, mixed with a quantity of vapour from the burning of the phosphorus, which renders it opaque, but which is soon absorbed by the water over which the experiment is made, leaving the gas transparent and invisible. This nitrogen is not, however, per-

fectly pure : for the burning of the phosphorus ceases be-
fore the oxygen is entirely consumed ; and nitrogen gas
appears also to have the property of dissolving a small por-
tion of phosphorus.   Other substances may be used, which
abstract the oxygen more completely ; a mixture of iron-
filings and sulphur, moistened with water, has this effect :
it was found by Priestley, however, that such a mixture,
after some time, gives out a small quantity of hydrogen
gas, which will mix with the nitrogen.   The liquor ob-
tained by boiling sulphur, with potash, or with lime, and
water, affords, on the whole, the best mode of procuring
pure nitrogen gas.   One part of it is inclosed in a bottle
or tube, with 5 or 6 parts, by measure, of atmospheric air;
they are frequently agitated, and the vessel being inverted
in a portion of the liquor, the air is exposed to its action
until it suffer no farther diminution of volume.   By this
liquid the whole of the oxygen of the atmospheric air is
absorbed, and nothing is added to the remaining nitrogen
gas ; at least, by agitating it with a little water, a slight
fœtid odour which it acquires from the liquid, and which
might be supposed to denote some impurity, is removed,
without any sensible diminution in its volume.

There are other processes by which this gas may be pro-
cured.   It is a constituent principle of animal matter.   If
a few pieces of flesh or muscular fibre be put into a retort,
and nitric acid diluted with 4 or 5 parts of water be add-
ed, on applying a moderate heat, nitrogen gas is disen-
gaged.   But there is reason to believe, that the gas obtain-
ed in this process is not perfectly pure, but holds a little
carbon dissolved.

Nitrogen gas is permanently elastic, invisible, insipid,
and inodorous.   It is lighter than oxygen gas, its specific
gravity being to that of atmospheric air, according to La-
voisier, as 966 to 1000; according to Kirwan as 985 ;
and according to Biot and Arago 969 ; to that of water
as 1.0000, it is .001189 ; 100 cubic inches of it weigh, at

the temperature of 55, and the barometrical pressure of 30, 30.40 grains.

This gas has no striking property, physical or chemical, by which it can be characterized : it is distinguished rather by negative qualities.

1st, It is incapable of supporting combustion. A burning body immersed in it is instantly extinguished.

2d, It is incapable of sustaining animal life by respiration. An animal put into a jar of it is immediately killed.

3d, It is not inflammable, or it cannot be made to burn. It combines, however, with oxygen gas. but this combination is not analogous in the phenomena it presents, to the combination of combustible bodies with that principle. It takes place very slowly, even when aided by the agency of an ignited or an electric spark ; and during the combination no light is disengaged, nor is any sensible heat produced. Hence the process cannot be termed Combustion.

Lastly, Nitrogen gas is not sensibly absorbed by water. If a jar filled with it be placed in water, it suffers no sensible diminution of volume. Dr Henry, however, has found, that when it is exposed for some hours to water, freed from the portion of air which water holds dissolved, 100 cubic inches absorb at the temperature of 60°, and under the usual atmospheric pressure, 1.47 cubic inches : the quantity, according to Dalton, amounts even to 2.5.

As affording the best method of distinguishing nitrogen gas from other gases which resemble it in general properties, it may be added, that it produces no change in the vegetable colours; and that, when agitated with lime-water, it does not render it milky, nor is it absorbed by it in larger quantity than by pure water.

Nitrogen exhibits more distinctive characters in the combinations into which it enters. It unites with oxygen in several proportions, forming compounds extremely different in their properties. It combines with hydrogen, and it dissolves small portions of phosphorus, sulphur, and

carbon; lastly, it is an element in all the products of the animal system. In its gaseous form, it does not however exert very energetic affinities, and the large quantity of it in the atmosphere seems principally to dilute the oxygen gas.

Several opinions have been proposed with regard to the nature of nitrogen gas. Priestley, in distilling water from earthen retorts, or through earthen tubes at a high temperature, found a large quantity of air to be produced, which appeared to be principally nitrogen, with a variable proportion of oxygen. He concluded, that the water is converted into air; and a similar opinion was afterwards supported by experiments of the same nature by some of the German chemists, Westrumb, Wiegleb and Goettling; nitrogen gas being regarded as a compound of water and caloric, and water being held to be the ponderable base of it as well as of the other gases.

Priestley afterwards found, however, that when water is distilled through glass or metallic vessels, there is no production of air, not even when clay or fragments of the earthen ware which he had used in the first experiments were introduced into the vessel. From this it followed, that neither the earthen ware, nor the heat, had any share in the effect; and he concluded, that the appearance was owing to the porosity of earthen-ware retorts or tubes, in consequence of which the watery vapour escapes, and the external air enters *. This was confirmed by subsequent experiments of Deiman and of Von Hauch.

Girtanner maintained the opinion of nitrogen being a compound, from experiments, many of them similar to those which had been before performed; and he affirmed, in opposition to Priestley, that this production of nitrogen takes place when the water is boiled from a glass retort, or through a heated glass tube, in either of which a little

* Philosophical Transactions, vol. lxxiii.

clay, lime, or siliceous earth is put, or when an earthen retort or tube is used glazed externally, but not if the glazing is on the internal surface. He concluded, that the agency of these earths in converting water into nitrogen probably depends on their attracting oxygen from it; and hence he adopted an opinion which had been advanced by Mayer, that nitrogen is a compound of oxygen and hydrogen, differing from water in containing less oxygen. With these conclusions he connected, too, several extravagant speculations, such as that oxygen and hydrogen are the elements of which all bodies are formed [*], which threw discredit on his opinions; and the accuracy of his experiments were called in question, particularly by Berthollet and Lagrange, who repeated the greater number of them without obtaining the results which had been described [†].

There is another class of facts from which the existence of a relation between nitrogen and water has been supposed to be established. Priestley observed, that on boiling water freed as completely as possible from any air which it might hold dissolved, a little elastic fluid is disengaged, which he found to be nitrogen, and this as long as he continued the experiment. He farther found, that when water, which by repeated processes with the Torricellian vacuum had been as completely deprived of air as possible, was converted into ice by freezing, the ice, though transparent on the outside, was opaque towards the centre; and when again melted, small bubbles of air were disengaged from it. And when the freezing of the water was repeated, still the same extrication of air took place; and " though I repeated," says he, " this process ten or a dozen times with the same water, always letting out the air that was procured by freezing, presently after it was

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* Nicholson's Journal, 4to, vol. iv, p. 137, &c.
† Ibid. p. 371.

extricated, and before it could have been re-absorbed,
yet on exposing it to another freezing I never failed to
get more air ; and the harder the frost was, the more air
I procured." This air he collected, by freezing about
three ounces of water in a cylindrical vessel of iron, to
which was adapted a glass tube, the diameter of which was
about the fifth of an inch : " the last portion of air was as
great as any of the preceding ; so that there remained no
reasonable doubt but that air might be procured from the
same water in this manner *ad libitum ;* and having got
near two inches of air in the glass tube, I put an end to
the experiment; and examining the air, I found it to be
wholly phlogisticated (nitrogen,) not being affected by ni-
trous air, and having nothing inflammable in it *."

From these, and his preceding experiments on the pro-
duction of air when water passes into vapour, Priestley
concluded, that water is convertible into nitrogen gas ; he
farther supposed a relation to exist between nitrogen and
hydrogen, in consequence of which the latter may be con-
verted into the former; and the whole series of facts he
considered as favourable to the hypothesis of water being
the basis or ponderable part of every kind of air, " the
difference between them depending on the addition of some
principles which we are not able to ascertain by weight."

The theory of these results is not yet perhaps satisfac-
torily elucidated, and the question, with regard even to
their accuracy, requires still to be made the subject of ex-
periment. In the present state of our knowledge, with
regard to nitrogen, it must be regarded as an undecom-
posed substance, and though there are some considerations
which lead to the opinion of its being a compound, we can
scarcely advance any conjecture having any precision as to
the nature of its composition. Berzelius has inferred from
speculations connected with the doctrine of definite propor-
tions, that it is a compound of oxygen with an unknown

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* Nicholson's Journal, 4to, vol. iv, p. 193.

combustible base, and has fixed the proportions at 44.32 of base and 55.68 of oxygen *. Others have affirmed, as a consequence of the same doctrine, that nitrogen can contain no oxygen,—a proof of the little value of such speculations. Mr Miers has revived the opinion of Girtanner, that hydrogen is the base of nitrogen,—forming it by combination with oxygen. On the principles of the atomic theory, he has assigned the proportions nearly the same as those given by Berzelius: And he has added a series of experiments in confirmation of the opinion †, but with results too complicated and uncertain to establish the conclusion. Davy found, that potassium aided by intense heat produces no change on nitrogen gas.

CHAP. III.

OF ATMOSPHERIC AIR.

The elementary nature of atmospheric air, a dogma handed down from the ancient philosophy, was universally admitted by the chemists. Mayow had called it in question; but his conjectures, not thoroughly established, and imperfectly understood, were not regarded. To Scheele the honour is due of having discovered the composition of the atmosphere. In 1775, as appears from the preface of Bergman to Scheele's treatise, he had observed the facts by which this is established, and drawn from them the just conclusion. Lavoisier claims the same discovery. He obviously had views, more or less clear, of the composition

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* Annals of Philosophy, vol. ii, p. 276.
† Ibid. vol. iii, p. 364,—vol. iv, p. 180.

of the atmosphere, suggested by the experiments which he performed in 1774 and 1775 * ; and in memoirs which he presented to the Academy of Sciences in 1776 and 1777, it is distinctly announced †.

Scheele's first experiment, by which he was led to the discovery of the constitution of the atmosphere, consisted in putting 4 ounces of the liquor prepared by boiling a solution of potash with sulphur in a bottle of the capacity of 24 ounce measures, closing the bottle accurately, inverting it in water, and allowing it to remain in this situation for two weeks, 20 ounce measures of atmospheric air being thus exposed to the action of the liquor. At the end of this period, on withdrawing the cork of the bottle under water, a portion immediately rushed in, shewing that a diminution in the volume of the inclosed air had been effected ; and this by measurement was found to amount to six parts in the twenty ‡. Various other substances he found to produce a similar diminution, as did also the burning of some inflammables. And on examining the residual air, he found it to be changed in its qualities, —to be lighter than atmospheric air, and to be incapable of supporting combustion §.

How are these phenomena to be explained ? Scheele was enabled to give the just explanation, by his previous discovery of oxygen gas. He had observed its property

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* Physical Essays, p. 297, 346. Mémoires de l'Acad. des Sciences, 1775, p. 525.

† Mémoires de l'Acad. des Sciences, 1777, p. 69, 195.

‡ This diminution is greater than could have arisen from the abstraction of oxygen ; and there is reason to believe, from the observations of Dr Austin, that, from the long exposure of the air to the liquor, part of its nitrogen had been abstracted, and combining with hydrogen from the solution, had formed ammonia.

§ Scheele on Air and Fire, p. 7, &c.

of supporting combustion in a degree so superior to atmo-
spheric air: finding, that, in the preceding experiments,
the atmospheric air is diminished in volume, he ascribed
this to the abstraction of some part of it, and farther find-
ing that at the same time it loses its power of supporting
burning, he concluded, that the portion abstracted is oxy-
gen gas, or what he named Fire Air; that atmospheric air,
therefore, is a compound of fire air, and of the air remain-
ing in these experiments, which is nitrogen gas.   This he
soon confirmed, by shewing that pure oxygen gas is totally
absorbed by the substances which, in his first experiments,
diminished the volume of the air, and that a mixture of
oxygen with nitrogen gas is affected in the same way as
atmospheric air.

Lavoisier inferred the composition of the atmosphere
from various processes, in which he observed, that its vo-
lume is diminished, and its qualities are changed; such
were the calcination of metals, the burning of phosphorus,
and other inflammables, and the action of nitrous gas.
When acquainted with the properties of oxygen gas, and
particularly its superior power of supporting combustion,
he concluded, that the diminution of volume, and the
change of qualities, is owing to its abstraction, and that
" the air of the atmosphere is composed of about one-
fourth of this gas, with three-fourths of an air mephitic and
noxious, and of a nature unknown *.

He afterwards performed an experiment by which the
composition of atmospheric air is more clearly demonstra-
ted.   Quicksilver was exposed to a heat nearly equal to
its boiling point, in a glass matrass with a bent neck con-
nected with a receiver containing atmospheric air.   A
red powder formed slowly on the surface of the quicksil-
ver, and the air diminished in volume; at the commence-
ment of the experiment the quantity contained in the ma-

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* Mémoires de l'Acad. des Sciences, 1777, p. 69.

trass and receiver was about 50 cubic inches; at the end
of it, it was reduced to between 42 and 43. Its qualities
were also changed, and, in particular, it was no longer ca-
pable of supporting combustion or animal life. The quan-
tity of red matter which had been formed on the surface
of the quicksilver was removed; it amounted to 45 grains;
on exposing it to a red heat in a retort, it returned to the
state of running quicksilver, which weighed $41\frac{1}{2}$ grains,
and between 7 and 8 cubical inches of air were collected,
which were oxygen gas. And on adding the oxygen gas
thus obtained, to the residual air of the first stage of the
experiment, an air was formed similar in its properties to
atmospheric air.

This experiment is an example both of the analysis and
synthesis of the atmosphere. The quicksilver heated in
atmospheric air attracts its oxygen ; the red substance
which forms on its surface is the product of this combina-
tion, and the residual air is nitrogen gas. At a higher
temperature,—that of a red heat, this compound is de-
composed, the repulsive agency of the caloric overcoming
the affinity; the oxygen assumes the gaseous form ; and
on adding the quantity of it thus obtained, to the residual
nitrogen, atmospheric air is reproduced.

The measurement of the quantity of oxygen contained
in atmospheric air, or indeed in any gas in which it is not
intimately combined, is named Eudiometry, from the sup-
position that it would indicate the goodness of the air, in
relation to its power of sustaining life by respiration. To
attain such a measurement, it is merely necessary to pre-
sent to atmospheric air, some substance which combines
with its oxygen, and which either does not afford any
gaseous product, or affords one that is easily abstracted
and measured. Different substances have been applied to
this purpose. The fluid employed by Scheele, in the ana-
lysis of the air,—the solution of sulphuret of potash, or,

sulphuret of lime, is perhaps superior in accuracy to any,
at least, if the air be not too long exposed to it, and be not
in too small quantity proportioned to the quantity of fluid.
Phosphorus is applied by a simple apparatus ; but by its
solubility in nitrogen gas, it adds to the bulk of the resi-
dual air, for which a correction must be made.   Nitrous
gas was used by Priestley ; it exhibits the result imme-
diately, but is liable to some sources of fallacy.   Hyd-
rogen gas exploded by the electric spark, with a given
volume of atmospheric air, likewise gives an immediate re-
sult, and, from the great diminution of volume in the mix-
ture, is susceptible of great accuracy.   The application of
these substances to this purpose will be stated under the
history of each.

It was once expected, that from the practice of Eudio-
metry, we should be able to ascertain the purity of air,
with regard to its salutary or noxious power on life.   It
was soon found, however, particularly by Priestley, (and
the fact has since been established by De Marti *,) that
the air of places the most offensive and unhealthy affords
as much oxygen as that of others of an opposite descrip-
tion : the air, for example, of crowded cities, of low damp
situations, or of crowded manufactories, has not been
found to contain less oxygen than that of the country.
The noxious quality of the air, in such situations, there-
fore, depends not so much on deficiency of oxygen, as on
the presence of effluvia not discoverable by analysis †.

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* Journal de Physique, tom. lii, p. 182.

† Lavoisier had found, that in a crowded assembly the air is
sensibly vitiated.   He collected a portion of the air in one of
the theatres at Paris towards the end of the performance, and
found it to contain a diminished proportion of oxygen, with
an addition of about 2 *per cent.* of carbonic acid ; and the air
in the wards of an hospital he found to be not less injured.
Mr G. Davy has lately stated some experiments, whence it
would appear that the air in the wards of a fever hospital did

The proportions of oxygen and nitrogen gases in atmospheric air have been variously estimated. Scheele supposed the quantity of oxygen to be more than 27 parts in the 100; and Lavoisier fixed the proportion at 27 by weight. Sennebier stated it to be 25. Priestley supposed it to vary from 20 to 25. Mr Cavendish supposed it to vary little, and to be not more than 20 in volume. There can be no doubt, that the higher proportions of oxygen are erroneous, and have arisen from inaccuracies in the eudiometrical methods from which they were assigned. By phosphorus, the diminution of volume in atmospheric air cannot be carried beyond 20 in 100 parts : by solutions of sulphate or muriate of iron impregnated with nitrous gas beyond 21; by detonation with hydrogen gas it is 21; and by a solution of sulphuret of potash, previously agitated with atmospheric air, to afford it a small portion of nitrogen, to which it seems to have an attraction, the diminution, as De Marti found by numerous experiments, is not greater than 22, or 21.5 by measure. If it be supposed, what is not improbable, that a little nitrogen is absorbed by the liquor, the proportion will be 21 by measure, or 23 by weight, leaving a residuum which is nearly pure nitrogen, of 79 by measure, or 77 by weight; and this corresponds with the results of other eudiometrical methods, as established by the experiments of Davy, Dalton and Gay-Lussac. Supposing a slight correction in this estimate, and considering the quantity of oxygen to be 20, that of nitrogen 80 *per cent.*, this would give the proportion of 4 to 1; and this again, on the assumption that atmospheric air is a chemical compound, would be conformable to the law, that gaseous bodies combine in simple

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not differ sensibly in the proportion either of oxygen or of carbonic acid gas from the external atmosphere. (*Annals of Philosophy*, vol. xi, p. 214.)

proportions estimated by their volumes. This analogy
has accordingly been pointed out as one favourable to the
opinion of its being a chemical compound, while, on the
other hand, the assumption of its being so has been con-
sidered as rendering it probable that this is the real propor-
tion *. No other analogy, however, confirms this suppo-
sition, and the entire want of those striking changes of
properties which attend those intimate combinations in
which this law is most distinctly observed, precludes much
weight from being attached to the argument. From ex-
periments too, made in reference to this, it appears, that
the proportion of oxygen cannot be estimated at less than
0.21†; and from others, executed by T. Saussure with great
care, to determine if the composition of the atmosphere
were uniform, the variations were found to vary only from
20.6 to 21‡.

It was at one time imagined, that the composition of at-
mospheric air is not uniform, but that it varies both at dif-
ferent parts of the earth's surface, and still more at differ-
ent heights. Ingenhousz made a number of experiments
to prove the former fact, from which he concluded, that
the air contains more oxygen at sea than on land, and
that in the neighbourhood of marshy situations it contains
less than the standard ‖. Saussure inferred from experi-
ments on the air at some of the most elevated parts of the
Alps, the summit of the great St Bernard, the Buet, &c.
that the proportion of oxygen is less than in the air on the
plains §. Von Humboldt relates, that air brought from a
great height in the atmosphere, by a person who had as-
cended in a balloon, contained in 100 parts 25.9 of oxy-

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* Annals of Philosophy, vol. vi, p. 321.   † Ib. vol. viii, p. 231.
‡ Annales de Physique, t. ii. p. 202.
‖ Philosophical Transactions, vol. lxx, p. 354.
§ Voyages, t. ii, p. 357.; t. iv. p. 451.

gen, while air at the surface contained 27.6 ; and that at
the summit of the Peak of Teneriffe, the proportion of
oxygen amounted only to 19, while at the foot of the
mountain it was 27. There is reason to believe, that all
these results are incorrect. The analysis of the air in the
upper regions of the atmosphere has been executed with
accuracy by Gay-Lussac and Thenard. A glass globe
was filled with air at the height of 21,735 feet from the
surface, the greatest which has yet been reached, and
when opened under water by Gay-Lussac after his de-
scent, one-half of its capacity was filled by the water,—a
sufficient proof that it had been accurately closed. The
air was subjected to trial, both by Volta's eudiometer, and
by the solution of sulphuret of potash ; it afforded by the
former method 21.49 of oxygen in 100 ; by the latter
21.63. Atmospheric air at the surface, analysed at the same
time in the eudiometer of Volta, gave precisely the same
result, 21.49 *. Saussure *junior* also found, that the air
on the summit of the Col du Geant contained within one-
hundredth part as much oxygen as that on the plain, and
even this difference may be ascribed to the difficulty of
making the experiment with perfect accuracy. The uni-
formity of the composition of the atmosphere at different
parts of the earth's surface appears also to be established.
Mr Cavendish observed, that air subjected to examination
at different times, and air likewise from different places, was
of perfectly similar composition † ; and the same observa-
tion had been made by Fontana ‡. Mr Davy could dis-
vover no sensible difference in the air sent from the coast
of Guinea and the air in England ‖. Berthollet found,
that the air in Egypt and in France was similar, affording

* Nicholson's Journal, vol. x, p. 286.
† Philosophical Transactions, vol. lxxiii, p. 129.
‡ Ibid. vol. lxix.
§ Journals of the Royal Institution, vol. i, p. 48.

22 of oxygen in 100, any difference observed amounting
not to a two-hundredth part of the air submitted to trial [*].
De Marti, by experiments in Spain, obtained the same
uniformity of composition in the air at places at a distance
from each other ; and he adds also, as established by his
experiments, that in every state of the atmosphere, whe-
ther with regard to temperature, to pressure as indicated
by the barometer, to winds, to humidity, to the season of
the year, or the hour of the day or night, the results were
precisely the same [†].   And the researches of Humboldt
and Gay-Lussac, made with the view of determining this
question, have established the same conclusion [‡].   What
is still more singular, and what sufficiently proves that no
great deterioration of the atmosphere from natural pro-
cesses is to be expected, is the result established by nu-
merous experiments, that little vitiation of the atmosphere
can be discovered even where it is exposed to causes by the
operation of which its composition must be changed. Hum-
boldt and Gay-Lussac found, that the air in a crowded thea-
tre was scarcely sensibly altered, after three hours, in its
composition, the proportion of oxygen being from 20.2 to
20.4, while that of the atmosphere was 21. Seguin likewise,
in submitting the air of the wards of hospitals to trial, which
had been kept closed for twelve hours, and which had an
insupportable odour, found it nearly as pure as atmosphe-
ric air. And Fontana had obtained the same result [§].
This proves that any change in the constitution of the at-
mosphere is quickly removed by its great mobility and
the diffusibility of its constituent gases ; and the noxious
qualities of confined or vitiated air must be referred to the
presence of effluvia not discoverable by chemical trials.

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[*] Memoirs relative to Egypt, p. 326.
[†] Journal de Physique, t. lii, p. 173.   [‡] Ib. t. lx, p. 152.
[§] Ibid. t. lxii, p. 101.

The insalubrious quality of the atmosphere, in particular
natural situations, must be ascribed to a similar cause.

In the constitution of the atmosphere there is a strik-
ing singularity. Its ingredients, though of different spe-
cific gravities, do not separate, and it is every where of
uniform composition,—a fact which appears to lead to the
conclusion, that its principles are chemically combined.
But, on the other hand, it has no qualities different from
those of its constituent gases, nor do these appear to be al-
tered, farther than by mere dilution. In presenting them,
too, to each other, they mix equally well, and remain per-
manently diffused in every proportion, and no change of
temperature indicates any intimate chemical action. Yet
under other circumstances they obey the usual laws of at-
traction, enter into intimate union, and form compounds
endowed with peculiar properties.

On either side, therefore, there appears a difficulty. If
these gases are retained in union by no mutual attraction,
why do they not separate, from the difference in their spe-
cific gravities ? If they are united by any attraction, why
is this not marked by the usual consequences of chemical
action, a change of temperature at the time it happens,
and a change of properties? This difficulty frequently en-
gaged the attention of chemists, and some were disposed
to regard the union between the gases, composing the at-
mosphere, as of a chemical nature, others as mechanical,
without giving any satisfactory explanation of the facts
that appeared adverse to either opinion. Mr Dalton at
length proposed a theory of the constitution of mixed
gases, entitled to the praise of great ingenuity, and which
explains the constitution of atmospheric air on the princi-
ple that it is a mechanical mixture, and at the same time ac-
counts for its constituent gases remaining uniformly mix-
ed.

Mr Dalton's hypothesis rests on two assumptions : 1st,
That the particles of any individual gas repel each other,

a fact of which there can be no doubt. 2dly, That the
particles of mixed gases neither attract nor repel, but are
perfectly indifferent, and not affected by their mutual
proximity.   From these principles it follows, that if two
gaseous fluids are mixed together, though of different spe-
cific gravities, they will soon be diffused, and intimately
mixed, and will remain so without any tendency, under
the circumstances in which they exist, either to separate
or to unite.   Each gas, from its own elasticity, or the re-
pulsion between its particles, diffuses itself over the space
in which they are confined : by the hypothesis, its parti-
cles exert no attraction to those of the other, there can
therefore be no chemical union : by the same hypothesis,
they do not repel those of the other, there is therefore no
cause to alter the arrangement which each would assume,
or every gas is as a vacuum to every other.   Hence is ex-
plained the constitution of the atmosphere.   Suppose that
on the earth's surface there rests a column of oxygen gas ;
this, from its elasticity, will rise to an indefinite height,
becoming less dense as it recedes from the surface, as being
subjected to less pressure.   If, on the same surface, a co-
lumn of nitrogen gas rest, its particles will equally recede,
and will be intimately mixed with those of the oxygen ;
other gases, carbonic acid for example, or watery vapour,
may be present, and will be arranged in the same man-
ner ; and thus, on the same surface, will rest so many co-
lumns of gases, each intimately blended, but neither act-
ing on, nor acted upon by the others, supported by its own
elasticity, and the inferior strata of each pressed only by
its own incumbent particles. Such may be the atmosphere
surrounding the earth, at least on such an hypothesis may
be explained the apparently discordant facts, that the gases
composing it do not separate, but remain uniformly mix-
ed, while, at the same time, they shew no marks of having
entered into chemical union.

    It is even contended by Mr Dalton, that such must be

the constitution of the atmosphere. Only one of three
suppositions can be admitted,—that the particles of mixed
gases attract each other,—that they repel each other,—
that they neither attract nor repel : were the first true,
they must, he conceives, be brought into union, which
would be discovered by the usual consequences of chemi-
cal combination ; were the second just, they must separate
if of different specific gravities, and the heavier fall to the
under part of the space they occupy. Neither of these is
the case with regard to the airs composing the atmosphere,
and hence he conceives must follow the third principle, on
which his hypothesis rests [*]. This hypothesis, he farther
applies to explain the constitution of all mixed gases, the
particles of which are not in intimate chemical combina-
tion.

Notwithstanding the apparent strictness of this reason-
ing, more is perhaps involved in it than what necessarily
follows, and a view of the constitution of the atmosphere
may, I believe, be delivered, in conformity to the principle,
that the elastic fluids composing it exert a mutual attrac-
tion. It is only necessary to admit, that chemical affinity
may be exerted between the particles of mixed gases, so as
to prevent their separation, but not with such force when
they are merely mixed as to bring them into intimate com-
bination. The particles of oxygen and nitrogen gases have
a mutual affinity, for they can be intimately combined.
At the temperature at which they exist in the atmosphere,
this is not sufficient to overcome their elasticity, and unite
them so as to detach their caloric, and form a new sub-
stance. But it may not be entirely dormant, but may be
so far exerted, as to prevent their separation, or even pro-
duce a degree of approximation, so inconsiderable, as not
to be discovered by any sensible change of volume.

The fallacy, it appears to me, in Mr Dalton's reason-

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[*] Manchester Memoirs, vol. v, Part II.

ing, is the assumption, that if chemical attraction be exerted between the particles of bodies, it must cause their intimate combination, and form a substance possessed of new properties; and that where such a combination does not happen, we have no reason to infer the existence or the exertion of any attraction. Now this does not appear to follow from any just view of chemical affinity, and it will be found inconsistent with a number of chemical facts. Chemical combination does not arise merely from the exertion of one force: several powers have generally operated before it has been effected, and its completion is owing to the predominance of one power over others which have opposed it. In the solution of a solid, for example, there are opposed the force of affinity between the solid substance and the solvent, and the cohesion of the solid retaining its particles in aggregation. If the former predominate over the latter, the solution takes place; if the latter be more powerful, no solution happens. But, even in this latter case, the affinity of the liquid to the solid has been exerted, though with inadequate force. The proof of this is, that if the cohesion be overcome by other means, the combination will take place. It happens, sometimes, for example, when the force of aggregation has been overcome by mechanical means, and still more when it has been weakened by the operation of heat. These causes do not give rise to attraction; they only favour its exertion by removing a force which counteracts it. Of course chemical attraction may exist, and may even be exerted to a certain extent when intimate combination does not take place.

This conclusion follows, not less strictly from considering the circumstances which influence the exertion of attraction between the particles of elastic fluids. When two gases combine intimately, the combination is not owing simply to the affinity exerted between them, but to the preponderance of this affinity over the elasticity which op-

posed their union; and, on the other hand, when two gases do not unite, this is no proof that they have no attraction to each other, or that this attraction is not exerted, but merely that it is not exerted with sufficient force to overcome their elasticities. If such an attraction exists, it must have been exerted, although from the predominance of the opposing circumstance, it has not become effective; and we thus arrive at the conclusion, that between mixed gases, which are capable, under any circumstances, of combining, an attraction must always be exerted with at least some degree of force, should even those circumstances, which are necessary to their intimate union, not be present, and, of course, that union not take place. It is under this point of view that I have considered this weak reciprocal action of gases. A similar view has been stated by Berthollet *.

We accordingly find, that from the different degrees of energy with which these forces are exerted, numerous shades of combination, and some of them accompanied by no change of properties, and scarcely by any condensation, are effected. In the solutions of salts in water, the attraction exerted is merely sufficient to give fluidity to the solid, and to counteract its cohesion and specific gravity; the properties are not altered, and, in many cases, so little is the condensation, that the enlargement of volume from the liquefaction counterbalances it, and the density is that of the mean density, or even sometimes less; and in the solutions of various vegetable principles, in water or alkohol, no change of density is perceived. It may equally be concluded, that such weak attractions may be exerted between aëriform bodies,—attractions sufficient to counteract their elasticity, and difference of specific gravity, without being sufficiently energetic, to cause an intimate combination. And this principle explains the constitution of the atmosphere. An attraction of this kind may be exert-

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* Chemical Statics, vol. i, p. 198.

ed between the particles of oxygen and nitrogen gases, may counteract the difference in their specific gravities, and prevent them from separating from each other; and thus may be accounted for the two facts which, on former hypotheses, appeared incompatible,—the uniformity of the composition of atmospheric air, and its having no properties different from those of the gases of which it is composed.

There appears to me sufficient evidence to prove that the principle of this theory is more just than the one Mr Dalton has proposed. Although the assumption, that mixed gases neither attract nor repel each other, may afford an explanation of the constitution of the atmosphere, it is not attempted to be established by any proof, nor is there any principle from which it can be inferred. The repulsion between the particles of any individual gas is owing to the operation of caloric, and is a necessary attribute of the form in which it exists; and why should there not be the same repulsion between the particles of two bodies in this form? What cause can counteract it, but a chemical attraction exerted between them? Besides, if there is no repulsion between the particles of different gases, as Mr Dalton conceives, what prevents them from entering into combination when they approach within short distances, as they must frequently do in the internal movements of a mixed elastic fluid? And if there exist no mutual attraction, how are they, under any circumstances, as, for example, by compression or by elevation of temperature, brought to combine? It may be added, that were Mr Dalton's hypothesis just, two elastic fluids ought in every case to diffuse themselves in any space, and mix equally with the utmost rapidity, each being as a vacuum to every other. Yet this facility of mixing is much dependent on their specific gravity.

Atmospheric air has been hitherto considered, as if it were composed only of oxygen and nitrogen gases. Another gas, carbonic acid,—the Fixed Air of the old nomen-

clature, is always found in it. It is discovered by exposing to the atmosphere substances which attract and combine with it at natural temperatures. Thus, if lime-water be exposed, the lime dissolved in the water attracts the carbonic acid in the atmosphere, and forms a compound, which, being insoluble in water, appears as a pellicle on the surface, and augmenting, breaks and falls to the bottom. The quantity is inconsiderable, and is not easily ascertained with accuracy. That it is inconsiderable, is evident, since tincture of turnsol, which is reddened by this gas, receives no tinge when a small quantity, a cubic inch, for example, is agitated for a long time with a large quantity, 700 or 800 cubic inches, of atmospheric air, as Fontana long ago remarked. It used to be estimated at 1 in 100; but this is a proportion undoubtedly too large. Mr Dalton, from an experiment, supposes it not to exceed 1 in 1000. He finds, that if a glass vessel filled with 102,400 grains of rain-water, be emptied in the open air, and 125 grains of strong lime-water be poured in, the mouth closed, and the vessel agitated, this portion of lime-water is saturated by the carbonic acid in this quantity of atmospheric air. But 125 grains of the lime-water used, he found, required for saturation 70 grain measures of carbonic acid gas; this quantity of carbonic acid, therefore, it may be inferred, is contained in 102,400 grain measures of atmospheric air, or the proportion by measure is $\frac{1}{1400}$th of the whole, which, from the relative specific gravities of carbonic acid gas, and atmospheric air, is by weight very nearly $\frac{1}{1000}$th *.

As carbonic acid is produced by respiration, combustion, and other processes at the surface of the earth, it has been supposed that the quantity of it in the atmosphere is derived from these sources. Such may be, and probably is its origin. At the same time, from the reciprocal at-

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* Manchester Memoirs, new series, vol. i, p. 254.

traction which gases exert, it is uniformly diffused; its proportion, so far as it can be ascertained, is always nearly the same; and though of greater specific gravity than the other gases in the atmosphere, it is found at the greatest heights, and at a distance from any immediate source of this kind, Saussure having found it in the air at the summit of Mont Blanc *; and Von Humboldt, in air brought down from a great height in the atmosphere by means of a balloon †. Mr Dalton found that the air in an assembly, in which two hundred people had breathed for two hours with the windows and doors shut, contained little more than 1 of carbonic acid in 100; and a similar result was obtained by Gay-Lussac and Seguin. Th. Saussure has lately stated the result of experiments, whence it appears that the proportion of carbonic acid in the atmosphere is larger in summer than in winter. He ascertained the quantity by saturating water of barytes in a large glass globe containing air. In winter, the quantity contained in 10,000 parts is 4.8 by measure, or 7.28 by weight; in summer 7.13 by measure, or 10.83 by weight. Saussure's experiments, however, were suggested by the preconceived opinion, that there must be a larger quantity of carbonic acid in the atmosphere in summer than in winter, from its greater production, during the former season, by the fermentation of vegetable mould at the surface of the earth. Gay-Lussac has shewn, that the increased quantity assigned by Saussure's results, if considered as arising from this cause, would require a consumption of carbonaceous matter to afford it far beyond what can be supposed, and has justly remarked, that the experiments require to be confirmed ‡.

A portion of Aqueous Vapour always exists in the at-

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* Voyages dans les Alpes, tom. vii, p. 323.
† Philosophical Magazine, vol. i, p. 333.
‡ Annales de Physique, tom. ii, p. 199.

mosphere, evidently derived from the evaporation of wa-
ter at the surface, and varying in its quantity according to
temperature, and other circumstances. The quantity at
any given temperature and pressure it is note asy to de-
termine with accuracy. The maximum was fixed by
Saussure at 10 or 11 grains of water in a cubic foot of air
at the temperature of 65°, and under a medium pressure*;
others have stated it higher. Saussure's result has been
confirmed, however, by the experiments of Flaugergues,
who has farther stated, that the maximum at 77° of Fah-
renheit, is about 16.7 grains, and at 43°, is 4.5 grains.
These proportions will give the quantity of 2.6 grains to
saturate air at the temperature of 32°. Mr Dalton, with-
out determining the greatest quantity, observes, that it va-
ries considerably, principally according to temperature.
In the torrid zone it is capable of exerting a pressure on
the surface of the earth equal to from 0.6 to one inch of
mercury; in our climate it rarely amounts to a pressure
of 0.6, and in winter is sometimes so low as 0.1. He sup-
poses that at the temperature of 55°, the force of vapour
in the atmosphere at an average is equal to .443 of mer-
cury, or nearly $\frac{1}{70}$th of the whole atmosphere†.

While the vapour in the atmosphere preserves the aërial
form, the air is transparent : even in this state, however,
it can be discovered by the action of substances which,
having a strong affinity for it, imbibe it when exposed to
the atmosphere. Thus lime exposed to the driest air soon
slakes, an operation owing to its combination with water.
When the vapour is condensing, it communicates to the
atmosphere a degree of opacity from the conglomeration
of particles of water. This, according to the extent to
which it happens, gives rise to the natural appearances of
clouds, mist, and rain.

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* Essais sur l'Hygrometrie, p. 141, 185.
† Manchester Memoirs, new series, vol. i, p. 253.

Spontaneous Evaporation, as the natural process by which water is elevated in vapour in the atmosphere is termed, is promoted by various causes. It takes place with more rapidity as the temperature is high ; hence it is greatest in warm climates ; it is favoured by a dry atmosphere, and by agitation and quick removal of the air ; hence the drying effect of winds. By this addition of watery vapour to the atmosphere, its elasticity is augmented, it becomes lighter, and the portion of air receiving it therefore ascends *.

Various kinds of instruments have been invented, named Hygrometers, to denote the state of the air with regard to dryness and humidity. The greater number of them have been constructed on the property which many bodies, those, in particular, of organic structure, have of attracting water from the air, and thereby suffering enlargement of volume ; a substance of this kind being selected, which is easily affected by slight variations of atmospheric humidity, and a mechanical contrivance being connected with it, so as to render its changes of volume sufficiently apparent. Such are the hygrometers of De Luc and Saussure, the former consisting of a fine slip of whalebone, the elongation or shortening of which is shewn by an index attached to it, turning round a scale of equal degrees from the extreme of humidity to that of dryness : in the latter, a human hair is applied in a similar manner. All instruments of this nature, however, are with difficulty constructed uniform and accurate, from the difficulty of fixing, with certainty, the extreme points ; their indications too do not at once attain the stationary point ; and they seem, in the course of time, to suffer some change of structure, whence the indications cease to correspond precisely with the original adjustment to the scale. The hygrometer of Mr Leslie is founded on a different principle. It is the

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* Philosophical Transactions, vol. lv, p. 116.

differential thermometer, (described vol. i, p. 209,) one of the balls of which is covered with silk, or fine cambric paper, and when the observation is to be taken is moistened with pure water. Evaporation takes place, which causes diminution of temperature, which is marked by the scale attached to the opposite leg. The cooling will be proportional to the rapidity of evaporation, and this will be greater as the air is drier; hence the degrees on the scale are adapted to indicate the relative dryness of the surrounding atmosphere. In a very short time, two or three minutes, the full effect is produced, and continues so, as long as water is supplied to support the evaporation. How far the indications of this instrument correspond with the real states of dryness or humidity, or how far the process whence they are inferred is liable to be affected by other circumstances, does not seem to have been made the subject of much investigation.

Different theories have been proposed, to account for the elevation of water in vapour, and its suspension in the atmosphere at natural temperatures. According to the theory of Halley, afterwards illustrated by Le Roy, Franklin and Hamilton *, spontaneous evaporation is the effect of a solvent power exerted by air to water. According to Saussure, the water is converted into vapour by the agency of caloric, but the vapour thus formed he supposed to exist in the atmosphere, combined with its constituent gases; and lastly, according to De Luc, and also in conformity to Mr Dalton's views, water is elevated in vapour solely by the agency of caloric, and exists in the atmosphere in mechanical mixture or diffusion.

According to the first of these hypotheses, water passes into vapour at common temperatures, and under a common atmospheric pressure, from the attraction exerted to it by the air, or rather by the gases composing the atmo-

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* Philosophical Transactions vol. lv, p. 146.

sphere, and is preserved in the state of vapour by this mutual attraction. The process was compared by Halley to the solution of a salt in water; the air dissolving the water as water does a salt, the solvent power in both cases being increased by heat, and the matter dissolved being separated or precipitated when the temperature is reduced. Other analogies were pointed out in favour of the theory; such as the acceleration of evaporation by a current of air, this renewing the solvent, and of course preventing that approach to saturation which would take place in quiescent air, and which, in conformity to the usual law of chemical attraction, would impede the solution. The increase of evaporation, in a given quantity of water, by enlarging its surface, was explained on the same principle, as it is thus more freely acted on by being more exposed to the attraction of the solvent. And, lastly, in support of the principle of this theory, it was observed, that a chemical affinity does exist between air and water, since not only is the latter combined with the former, but a portion of air is likewise combined in water, and retained by a considerable force.

One fact, however, led to an opposite view. Water, even at the common temperature of the atmosphere, is found to pass into vapour *in vacuo*. Thus, in the vacuum of the air-pump, it evaporates perceptibly at 70° of Fahrenheit; and Mr Watt shewed, that at lower temperatures, and in the more perfect Torricellian vacuum, the same evaporation takes place. A drop of water was admitted into the column of mercury in the barometer, at the temperature of 57°. On rising to the surface of the quicksilver, vapour was formed, which by its elasticity depressed the mercury half an inch. Since it is proved, therefore, that water passes into vapour *in vacuo*, it was concluded, that its spontaneous evaporation, under exposure to the atmosphere, is not owing to any action of the air, but merely to the agency of caloric. Two modi-

fications of this opinion were proposed. By Saussure, the vapour, after it was formed and mingled with the atmosphere, was supposed to be chemically combined with it. By De Luc, it was supposed still to exist in the state of vapour uncombined, and merely intimately mixed or diffused. In conformity to his views of the constitution of the atmosphere, Mr Dalton adopts the latter hypothesis. Water, at every temperature, he considers as convertible into vapour by the sole operation of caloric: the vapour thus formed exists in the atmosphere in a distinct state, neither attracted nor repelled by the other gases, but supporting itself by its own elasticity, the quantity of it present being dependent on the temperature, and the amount of the pressure exerted by the quantity of vapour already formed.

If the discussion were confined to the two modifications of the opinion, that the conversion of water into vapour arises from the operation of caloric, the views already suggested on the constitution of the atmosphere would lead to the adoption of the hypothesis of Saussure, that the vapour is in a state of combination, not intimate, but such as must be produced by an attraction exerted towards it by the permanent gases; for if an attraction be exerted between these gases, it equally follows, that an attraction must be exerted between each of them and the watery vapour. But, independent of this, there are other considerations which render it probable, that the conversion of water into vapour is not owing to the operation of caloric alone, but is influenced by the affinity of air to water; that, therefore, the original theory of spontaneous evaporation is just.

There appears an obvious fallacy in the reasoning on which the opposite hypotheses rest, that because water passes into vapour *in vacuo*, at a natural temperature, it will pass into vapour, at least to the same extent, at the same temperature, under a common atmospheric pressure.

The pressure of the atmosphere diminishes or prevents the evaporation of other fluids. Why should it not have the same effect on water? and if it have, what proof is there that water under that pressure will pass into vapour, independent of the agency of the air? It is acknowledged, that atmospheric pressure alters the boiling points of fluids, or that it has a powerful effect in preventing the transition of substances into the elastic form. By placing water *in vacuo*, the chemical agency of the atmosphere is indeed removed, but its mechanical pressure is also removed; and nothing can be more gratuitous than the conclusion, that because it passes into vapour under the absence of this pressure, it will equally do so when subjected to it. The proper manner of making the experiment is to exclude the chemical agency of the air, while the pressure of it is preserved;—in other words, let water be placed *in vacuo*, under the pressure of a column of mercury 29 inches in height, which is equal to the pressure of the atmosphere. If in this case vapour were formed, the conclusion would be just, that spontaneous evaporation is independent of any chemical agency of atmospheric air. But the fact will be found very different; for, although water introduced into the tube of the barometer at 60°, passes into vapour, and depresses the mercury half an inch, that vapour will be completely condensed, and the water retained in the fluid form by a pressure a little greater, instead of being able to exist under the pressure which is equal to that of a column of mercury 29 inches high.

The force of this reasoning is sought to be obviated by a position maintained by Mr Dalton, that atmospheric pressure does not prevent the evaporation of liquids,—a position which appears to follow from his doctrine, that mixed gases do not repel each other; for suppose vapour to be formed from water, at a natural temperature, and to be diffused through the atmosphere, as according to that

doctrine it is neither attracted nor repelled by the contiguous gases, it will not be subjected to their pressure, and hence it will exist to the quantity of it which can be formed at that temperature independent of that pressure. Were, therefore, says Mr Dalton, every part of the atmosphere except the aqueous vapour instantly annihilated, little addition would be made to this aqueous atmosphere, because it already exists in every place almost entirely up to what the temperature will admit. But the difficulty is eluded, not removed. If water were converted into vapour, it would not, according to Mr Dalton's views, be condensed, since the gases composing the atmosphere are supposed to have no action on this vapour; and it may even be admitted, that the quantity of vapour formed, suppose the pressure of the atmosphere to be removed, would not be much greater than what at present exists in it; for that vapour would itself form an atmosphere, which, at a given temperature, can exist only to a certain extent, and which by its pressure would prevent the farther transition into vapour. But the difficulty in the hypothesis, is not how the vapour, were it formed, can exist uncondensed ; but how the transition of the water into vapour can be effected; and it still appears to me that this affords a demonstration of its fallacy. Elastic fluids press on the surface of liquids. This the barometer, syphon, and innumerable facts, demonstrate. The pressure exerted by the atmosphere is equal to that of a column of quicksilver $29\frac{1}{2}$ inches in height. Place water under the pressure of such a column, and indeed under one much less, none of it passes into vapour. How, therefore, if we exclude the agency of the affinity exerted to it, should it pass into vapour under the pressure of the atmosphere ? To avoid this difficulty, Mr Dalton has recourse to a singular supposition. He supposes, " that it is not till the depth of 10 or 12 strata of particles of any liquid, that the pressure upon each perpendicular column becomes uniform ; and that several of

the particles in the uppermost stratum are in reality subject to but little pressure *." It is evident that such a supposition is an accommodation to the hypothesis; and its improbability is not less apparent.

Mr Dalton supposes also, that the difficulty is the same on the opposite hypothesis. This however is not the case; for another power is introduced, the affinity of the atmospheric gases, which may overcome the pressure, and elevate a portion of the water in vapour : This affinity, Mr Dalton adds, is described as weak; and he presumes, therefore, that it is inadequate to this effect; but it is weak only when considered in relation to the opposing circumstances,—the elasticity of the gases of the atmosphere when they are to be absorbed by it, and the elasticity of the vapour when, in consequence of its exertion, water has passed into that form.

It appears to me, therefore, that the hypothesis is still liable to the original objection, that of resting on the conclusion both illogical and inconsistent with fact,—that if water pass at a certain temperature into vapour *in vacuo*, it will equally pass into vapour at the same temperature under the atmospheric pressure, independent of any attraction exerted to it by the air. Under that pressure, it may justly be inferred, water could not evaporate, were not this attraction exerted to it. Spontaneous evaporation, therefore, may be ascribed to this attraction, and the aqueous vapour existing in the atmosphere may be regarded as in the same state of weak combination, as that exerted between the permanent gases composing it. The only difference is, that they being so far distant from the point at which they assume the aëriform state are not affected by natural changes of temperature, while these changes must affect the combination so far as it relates to the aqueous vapour.

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* New System of Chemical Philosophy, p. 193.

It has been urged in support of the hypothesis of De Luc and Dalton, that at a given temperature the quantity of watery vapour in any gas is the same as that in any other. This was established by Saussure with regard to common air, carbonic acid gas, and hydrogen gas, at least he found that these gases, under similar circumstances, came to the same hygrometrical state *; and it has since been confirmed by the experiments of Clement and Desormes, the same quantity of water, according to these chemists, being taken up by all the gases under the same circumstances †. Now the fact is quite conformable to the opinion, that the formation of vapour depends merely on the operation of temperature, while, if it were owing to an affinity exerted by the gas, it might be inferred *a priori* that the different gases would exert attractions differing in force, and that therefore water would be dissolved in larger proportions by some than by others. The argument may even be placed under a stronger point of view; for it is affirmed, that the quantity of watery vapour in any gas is the same as that which would be contained in a vacuum of the same space as that which the gas occupies. This too was ascertained by Saussure, and has been established by De Luc and Dalton. It appears to prove, that the gases exert no affinity which causes the evaporation, or at least no affinity to the vapour formed, since if they did, this law would not be observed; and the fact that the vapour exists to the same quantity in a given space whether air be present or not, seems to shew, that that air exerts no attraction to it, but that the vapour exists as such from the operation of caloric alone.

It is not clear, however, that the fact is established. Saussure himself did not regard his experiments as proving that the same quantities of water are present in differ-

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* Essais sur l'Hygrometrie, p. 231.
† Annales de Chimie, t. xliii, p. 125.

ent airs, in the same hygrometrical state, for he distinguished properly between the saturation of airs with humidity, and the quantities requisite to produce that saturation. The proof given is, that the elasticity exerted by watery vapour in different airs at the same temperature is the same. A quantity of water is allowed to pass into vapour *in vacuo,* and its elasticity is measured by the depression it occasions in a column of mercury; this at 65 being such as to cause a depression of 0.5 inch: a quantity of dry air is put into a vessel of the same capacity as the vacuum, and a little water introduced, the temperature being the same; it passes into vapour, and the acquired elasticity is found to be the same as that in the vacuum, or at 65° will cause a rise in an included barometer of 0.5 inch; and if any other gas be substituted for atmospheric air, the result is still the same. Hence it is concluded, that the same quantity of water has been converted into vapour.

But it was justly observed by Mr Gough, that the elasticity exerted by vapour under these different circumstances is not a measure of its quantity, unless it be taken for granted, what is the point in dispute, that that vapour is uncombined. If the vapour be in a state of combination with the gases, this will restrain and limit its elasticity; and the more powerful the attraction exerted, the diminution will be greater; and hence it may happen, that at the point of saturation, or where the affinity is balanced by the elasticity, the same elastic force will be exerted in all these cases, though the quantities present may be different, and their force may be the same with that exerted by uncombined vapour at that temperature. The fact, therefore, experimentally proved, seems to follow as necessarily from this theory, as from the hypothesis that the watery vapour contained in a gas is in an uncombined state.

It has been attempted to be shown by another kind of experiment, that the quantities of water contained 'at the same temperature, and under the same pressure, in differ-

ent gases, are the same. When exposed to substances which have a strong attraction to water, they deposite, from equal volumes, the same quantity of humidity. This appears to be established by the experiments of Clement and Desormes. They exposed atmospheric air, oxygen, hydrogen, nitrogen, and carbonic acid gases, saturated with moisture, successively to muriate of lime, a substance which has a strong attraction to water, and found that the same quantities, or at least with differences so inconsiderable as might arise from the unavoidable imperfections of the process, were deposited,—the quantity amounting to about 6 grains from a cubic foot. But they were aware, that this is no proof that these gases, under the same circumstances, contain the same quantity ; for they observe, that it still " remained to know, whether the quantities of water which cannot be taken from water by desiccation, are equal ;" and they admit, that " it was almost impossible to ascertain this point by a direct experiment ;" nor indeed did they draw any conclusion but from analogy. It is sufficiently evident, that by such experiments, the question remains undetermined. The very difference in the strength of affinity, which may give rise to a difference in the quantity contained, will oppose proportionally an obstacle to any method by which it is to be abstracted. As one gas will contain more water than another, from exerting to it a stronger attraction ; so this superior attraction will enable it to retain a larger quantity when exposed to the action of substances having a tendency to abstract it ; and thus the different gases may deposite the same quantities, but still retain different quantities.

It is also to be observed, that the differences in the quantity of watery vapour in the different gases is probably not considerable ; perhaps even scarcely appreciable, owing to the weak energy of the action exerted. By their attraction to water, they convert it into vapour ; but the acquired elasticity renders the combination of the vapour

with the gas comparatively weak.   Hence, as the elastici-
ty is in all cases the same at the same temperature, as it
always counteracts the affinity, and as differences in the
forces of the affinities exerted by the different gases are in-
considerable, it must follow, that the difference in the por-
tion of water dissolved will be inconsiderable, and scarcely
capable of being estimated.

These facts, then, are not subversive of the opinion, that
spontaneous evaporation is owing to an affinity between air
and water.   Nor is there any difficulty attached to this
opinion.   It accounts for the phenomena, and is deduced
from just views of the relation between water and the gases
composing the atmosphere.   An affinity exists between
them, as is shewn in their absorption by water, in quanti-
ties compared with each other not regulated by the pres-
sure which is present : and the same affinity must give rise
to the solution of water by these elastic fluids.   The va-
pour existing in this state of slight combination is deno-
minated Hygrometric, to distinguish it from vapour sup-
posed to exist in some gases in intimate chemical union.

A question of considerable difficulty, with regard to the
watery vapour in the atmosphere, is that relating to the
causes of its condensation.   That it should be condensed,
and water deposited as the temperature is reduced, neces-
sarily follows ; but we do not observe that intimate con-
nection which we would look for between these two events,
and no very satisfactory theory has been delivered of that
rapid and copious deposition of water which constitutes
rain.

An hypothesis advanced by Dr Hutton on this subject
appeared to afford a satisfactory explanation.   Assuming
that evaporation is owing to the solution of water in air by
a chemical process, he observes, that this solution may pro-
ceed in three ratios with regard to temperature; it may vary
in the same ratio with the temperature, so that equal aug-
mentations of temperature in the air may be accompanied

with equal augmentations in the quantity of water dissolved; it may proceed in a greater ratio ; or, lastly, it may be in a less. In the first case, when two portions of air, at different temperatures, are mingled together, no condensation of vapour will take place, because the whole quantity of air is able to retain dissolved the quantities of water which each portion held in solution. If the increase of solvent power be in a less ratio than the rise of temperature, the mixed air will be capable of dissolving even more water if it were present. It is therefore only in the third case, in which the solvent power of the air increases in a higher ratio than the temperature is augmented, that the precipitation of any portion of water will take place. On the supposition of this being the case, it was conceived by Dr Hutton, that the formation of rain might be explained. When two quantities of air, one at a higher, the other at a lower temperature, each saturated with water, are mixed together, as they may be by winds and currents in the atmosphere, the mixed air will be unable to hold dissolved the whole of the water each portion had in solution ; hence a precipitation must take place. This if slow will form clouds or mist. If more rapid, and taking place at some height in the atmosphere, the resistance opposed to the descent of the particles of water will favour the exertion of the attraction of cohesion between them, and cause them to unite in drops, producing rain.

The only proof of this theory given by Dr Hutton was an analogical one, derived from the fact, that this law of the progression of solubility in an increasing ratio with regard to temperature, is observed in the solution of certain salts in water. This, however, is rather adverse to the hypothesis. The solution of a solid in a fluid is owing to the predominance of the affinity over the cohesion of the solid : an increase of temperature diminishes the cohesion progressively : the obstacle is thus becoming less as the temperature rises, and the solution ought there-

fore to proceed in an increasing ratio. But with regard
to evaporation, the condition is the reverse. The obsta-
cle to the mutual affinity between air and water is the
elasticity which the water, by passing into vapour, acquires
from that combination. By an elevation of temperature,
this elasticity is increased. Hence the obstacle to the com-
bination is becoming more powerful as the temperature
rises, and the evaporation ought to proceed in a decreas-
ing ratio, or the reverse of what Dr Hutton supposed.
The kind of combination, however, into which air and va-
pour enter, is so slight, that it will probably not be much
counteracted by an increase of elasticity; and an elevated
temperature augmenting the quantity of vapour which may
exist, it may give rise to the increasing ratio which Dr
Hutton supposed. That it increases at a high rate, has
been shewn by Mr Dalton, as has been already stated,
(vol. i, p. 276.) And Mr Leslie has also, from experi-
ments on the actual evaporation of water in air, inferred
the results. " By connecting the range of observations, it
would appear, that air has its dryness doubled at each rise
of temperature, answering to 15 centesimal degrees. Thus,
at the freezing point, air is capable of holding a portion of
moisture represented by 100 degrees of the hygrometer;
at the temperature of 15 centigrade, it could contain 200
such parts; at that of 30, it might dissolve 400; and, at
45 on the same scale, 800. Or, if we reckon by Fahren-
heit's divisions, air absolutely humid holds, at the limit of
congelation, the hundred and sixtieth part of its weight
of moisture; at the temperature of 59 degrees, the eighti-
eth part; at that of 86 degrees, the fortieth part; at that
of 113 degrees, the twentieth part; and at that of 140 de-
grees, the tenth part. While the temperature, therefore,
advances uniformly in arithmetical progression, the dis-
solving power which this communicates to the air mounts
with the accelerating rapidity of a geometrical series *."

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* Relations of Air to Heat and Moisture, p. 122, 123.

It is justly remarked by Mr Leslie, that the mixture of differently heated masses of air, with their respective portions of humidity, is insufficient alone to give rise to any very sensible precipitation of rain. It is necessary to have recourse to the mutual operation of currents of air at different temperatures, moving with rapidity in opposite directions, and mingling together. By this a large volume of the air is brought into contact in a given time. If, for example, the one current have a temperature of 50°, and the other that of 70, the mixture at their surfaces will attain the mean temperature of 60. According to the preceding law, the two will bring together 200, and 334.2 parts of moisture, making 267.1 parts for the compound, which, at its actual temperature, can hold only 258 6 parts ; the difference therefore, or 8.6, will be precipitated, corresponding to the 1860th of the whole weight of the mixed air. It would require a column of air, Mr Leslie continues, 25 miles in length, to furnish over a given spot, and in the space of an hour, a deposit of moisture equal to the height of an inch. But if the sum of the opposite velocities amounted to 50 miles an hour, and the intermingling influence of the two currents extended to not more than a quarter of an inch, there would be produced in the same time a fall of rain reaching to half an inch in altitude. Now this, he remarks, comes within the limits of probability, and agrees sufficiently with experience and observation ; and in higher temperatures, even with the same difference between the two currents, the quantity precipitated would be greatly increased.

It has frequently been supposed, that electricity is an agent both in the formation of aqueous vapour, and the production of rain. It is affirmed, that when it is communicated to water, it promotes its evaporation ; that the vapour and the fluid are in different electric states, and that the precipitation of rain is often connected with alterations of the electrical state of the atmosphere. But the

facts on this subject are either inconclusive, or not well as-
certained.   That electricity promotes evaporation, appears
to have been disproved by Van Marum.   He placed cups
of water and other fluids, accurately weighed, on an elec-
trical conductor connected with the machine, and similar
quantities were placed unconnected and at a distance from
it.   The former, after having had electricity communica-
ted for half an hour, were not found to have evaporated
more than the others *.

The atmosphere consists, then, of oxygen, nitrogen, car-
bonic acid, and aqueous vapour and the proportions Mr
Dalton remarks are nearly as follow :

Nitrogen gas,   77.5 by measure, 75.55 by weight.
Oxygen gas,   21 ——————— 23.32
Aqueous vapour,   1.42 ——————— 1.03
Carbonic acid gas,   .08 ——————— .10

Omitting the aqueous vapour which is variable in quan-
tity, the proportions of the permanent gases are stated by
Humboldt, from experiments by him and Gay-Lussac, at

Nitrogen gas,   0.787 by measure,
Oxygen,   0.210
Carbonic acid, 0.003

It has been imagined that a portion of hydrogen may
exist in atmospheric air. In the usual analysis of it, oxygen
is abstracted, and the residual air is nitrogen.   But it is
not proved that this nitrogen is perfectly pure; it is possible
that a portion of hydrogen may be mingled with it, which,
from not being considerable, may not be detected. If even
hydrogen be added to atmospheric air, in the proportion
of 6 in 100, it has been found by Humboldt and Gay-Lus-
sac that the mixture is not inflamed by the electric spark.
They have proved, however, that no sensible portion of
hydrogen is contained in atmospheric air, as, when a com-

* Philosophical Magazine, vol. viii.

parative analysis was made of common air, and of an arti-
ficial air, composed of 20 of oxygen and 80 of nitrogen,
each perfectly pure, by detonation with a measured quan-
tity of hydrogen, the results were in both the same [*].

Many other substances must be present in atmospheric
air, though in quantities too minute to be detected by che-
mical analysis. Not only do a number of bodies pass into
vapour at the surface of the earth from the effect of tem-
perature; but the air, by its action, promotes this vapori-
zation, and under exposure to it bodies pass freely into va-
pour, which, at the same temperature in vessels having an
imperfect communication with the air, do not evaporate.
This important fact, it has already been remarked, has been
established by Gay-Lussac [†].

The properties of atmospheric air appear to be merely
the aggregated properties of the gases of which it consists.
It is invisible, inodorous, insipid, compressible, permanent-
ly elastic. Its specific gravity is, according to Kirwan,
.0012279, or, according to the experiments of Sir G. Shuck-
burgh, .001208 at 60°, and under the barometrical pres-
sure of 30,—under that of 29.5.001188. 100 cubic inches
weigh 31, or according to the latter estimate 30.5 grains.
It supports combustion; and as it does so from the oxygen
it contains, the combustion is less rapid and vivid, and
continues for a shorter time than in oxygen gas. By the
same agency it supports animal life; a portion of its oxy-
gen is consumed in respiration, and converted into car-
bonic acid. It is very sparingly absorbed by water. The
absorption, too, is unequal, more of the oxygen being com-
bined with the water than of the nitrogen. Scheele ob-
served, that when agitated with water, the oxygen was ab-
sorbed in preference to the nitrogen; by using boiled wa-
ter, and agitating a small portion of air with a large quan-

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[*] Journal de Physique, tom. lx, p. 158.
[†] Mémoires de la Société d'Arcueil, p. 201.

tity of water, and keeping them in contact for a number of days, so much of the oxygen was absorbed, that the residual air extinguished a burning candle.

Atmospheric air is an important agent in many of the operations of nature. Besides serving as the vehicle of the distribution of water, it is, by its mobility, the principal agent by which temperature is in some measure equalized, or at least its extremes are moderated. Animals are immediately dependent on it for life. It is supplied by respiration; in the more perfect animals, its deprivation cannot be sustained for a few minutes; and even in the less perfect, the abstraction of it is followed, though not so immediately, by death. Its agency depends principally on its oxygen, a quantity of which is spent in every inspiration in producing chemical changes in the blood. Vegetable life is also in some measure dependent on it; it conveys water, and perhaps also carbonic acid, and even other principles, to the leaves of plants, and is thus subservient to their nutrition and growth.

An interesting subject, but one extremely obscure, relates to the natural processes by which the constitution of the atmosphere is preserved. By respiration, combustion, and other chemical changes going on at the surface of the earth, there is a constant consumption of its oxygen, and by many of these processes there is also a production of carbonic acid gas, by both of which its composition must be altered, and its purity considered in relation to animal life impaired. Yet we do not find that any sensible deterioration takes place; and indeed we have proof, from its adaptation to the processes of nature, that its composition must have been always the same. By what causes, then, is this uniformity of composition preserved? At one time it was imagined that the vegetable kingdom performed this important function; growing plants absorbing, it was supposed, carbonic acid by their leaves, and exhaling oxygen gas. The two tribes of animated beings appeared thus

to stand opposed to each other in their relations to the atmosphere, and this presented an admirable view of adjustment in the economy of nature. There is, however, much reason to doubt of the facts on which the opinion rests, and, from more recent investigations, it appears even, that except when under the direct action of the rays of the sun, vegetables, like animals, consume oxygen, and form carbonic acid. There must therefore be other processes by which the changes in the atmosphere are regulated, and its purity restored; and these are at present very imperfectly traced. B. Prevost has given a curious calculation to shew, that from the weight of the atmosphere, and the quantity of oxygen which exists in it, no perceptible change can be expected to occur even in an immense period, making the largest allowance that can be supposed for the consumption of oxygen from animal respiration, and other processes going at the surface of the earth;—the quantity consumed, at the largest calculation, not exceeding in 100 years the 7200th part of the whole weight of that gas, and the most accurate methods of analysis not being capable of detecting a variation much greater [*]. This shews that any apparent change must take place much more slowly than might at the first general view of the subject be supposed; but still it is obvious that in indefinite time the change must occur, and affect the system of nature, if not counteracted by causes equally constant in their operation.

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[*] Annales de Physique et Chimie, tom. iii, p. 100.

CHAP. IV.

OF THE CHEMICAL AGENCY OF OXYGEN IN ITS PURE FORM,
AND AS IT EXISTS IN ATMOSPHERIC AIR.

THE chemical agency of oxygen is more important than
that of any other principle; its affinities being more exten-
sive, and more energetic. These affinities are exerted by
it not only in its pure form, but likewise as it exists in at-
mospheric air, and this with nearly the same force, and
with similar results. It is even more generally as a con-
stituent part of atmospheric air that it operates as a che-
mical agent. I have therefore reserved the general view
of its chemical action until the constitution of the atmos-
phere has been explained. This view I have now to de-
liver.

The combinations of oxygen are often attended with the
extrication of light, and the production of heat, giving rise
to the phenomena of combustion. The illustration, there-
fore, of this important chemical process, belongs to the
statement of its general agency.

The phenomena of combustion, and the distinction of
bodies into Combustible or Inflammable, and Incombus-
tible or Uninflammable, are sufficiently familiar. The lat-
ter, when exposed to heat, have their temperature raised,
in proportion to the degree of heat applied to them; but
whenever this communication of caloric from an external
source is stopt, their temperature falls, and they return to
their former state. Combustible bodies, on the contrary,
when heated to a certain point, begin to suffer an evident

change; they become hotter than the surrounding bodies, emit light, and appear to be consumed, or, to speak more correctly, pass into a state of combination, whence products are frequently formed not apparent to the senses. It is this rapid emission of light and caloric, and this change of properties, and apparent loss of substance, which constitute the process of combustion.

Beecher proposed the first connected hypothesis to account for combustion. He supposed that there exists in combustible bodies a peculiar kind of matter, which he named inflammable earth, and that this put in motion exhibits the phenomena of heat and light. Stahl extended and refined this hypothesis. With Beecher he attributed the inflammability of bodies to a common principle; but this principle he did not conceive to be of an earthy or solid nature, nor did he suppose fire to be the effect of any peculiar motion. The inflammable principle he considered as being merely the matter of heat and light, pure fire, or, as he named it, Phlogiston. Combustion, therefore, is the disengagement of this principle: Inflammable substances are compounds of it with certain bases; and, when it is expelled, their inflammability is lost, and a substance is left possessed of different properties. Phlogiston he likewise supposed to be capable of being transferred from one body to another, without being rendered sensible by the appearance of heat or light; and by this transfer, the body which is deprived of it, suffers a change similar to that produced during combustion, while that which receives it acquires of course the property of inflammability.

In the original hypothesis, as Lavoisier has observed, there is little merit. It was easy to say, that inflammable bodies burn because they contain an inflammable principle. But it involves a general important fact, for the discovery of which we are indebted to Stahl, that the property of inflammability may be lost by a body, and restored to it by the agency of another, which loses it in its turn.

The hypothesis of Stahl being capable of being applied to a number of chemical phenomena, was universally a-dopted, nor for a considerable period was any doubt entertained of its truth. Founded, however, on an imperfect knowledge of the phenomena which it was designed to explain, its deficiency gradually became apparent. Stahl had overlooked the influence of the air in combustion, though even before his time it had been demonstrated by Mayow and Boyle. Of the necessity of its presence to support this process, the phlogistic doctrine gave no account. It had likewise been ascertained by experiment, that though in some cases the combustible body appears to be consumed during combustion, in others it increases in weight,—a fact equally inexplicable on the hypothesis, since the disengagement of phlogiston, from the inflammable body, ought rather to diminish its gravity, or, if it were too subtle to produce this effect, still no cause could be pointed out why the weight should be increased. This increase of weight had even been ascribed by Hales to the air which is absorbed; but this explanation seems to have been little attended to, and various attempts were made to solve these difficulties, in conformity to the doctrine of a phlogistic or inflammable principle, though with no great success.

At this time the experiments of Black, Priestley, Cavendish, and others, directed the attention of chemists to the influence of the air in combustion; and, from the facts which were discovered, various modifications of the doctrine of Stahl began to be proposed. Bayen and Lavoisier were the first chemists who doubted of its truth, so far at least as to explain some of the phenomena referred to it, on a different principle. Bayen had observed, in the formation of some metallic precipitates, an increase of weight, and with the view of ascertaining if this was owing to air combined with the metal, he endeavoured to discover, if, in reducing them to the metallic state, air was gi-

ven out. After various experiments, in which they were reduced by heating them with charcoal, and in which a large quantity of air was obtained, he succeeded in reducing the precipitates of mercury by heat alone, and observed, that, during the reduction, a large quantity of elastic fluid was obtained. From these results he concluded, that " the language of the followers of Stahl could be no longer held, and that they will be forced to restrict their doctrine with regard to phlogiston,—either to admit that these mercurial precipitates are not metallic calces, although some of their most celebrated chemists have considered them as such ; or that there are calces which may be reduced without the agency of phlogiston *." And again, these " experiments lead me to conclude, that in the mercurial calces, the mercury has its calcined state, not from the loss of phlogiston, but from its intimate combination with the elastic fluid, of which the weight added to that of the mercury is one of the causes of the increase of weight which I observed in the precipitates submitted to examination †.

Lavoisier has been said to have derived his system from these ideas of Bayen ; but the charge appears unjust : some of his researches on the same subject were prior, and are even referred to by Bayen, in his first memoir on the mercurial precipitates ‡. And he established with more precision, and to a greater extent, the facts on which the modern theory of combustion rests. He shewed (what had before indeed been observed by Boyle and Hales, though the observation had not been much attended to,) that in combustion, and the analogous process of metallic calcination, the air is diminished in volume, and that this diminution stops at a certain point. He proved, too, by experi-

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* Opuscules Chimiques, tom. i, p. 263, 282.
† Ibid. p. 228, 258.
‡ Journal de Physique, 1774.

ment, a fact before partially known, that the substances subjected to such processes increase in weight; and he observed, that in the reduction of metals, a quantity of air is given out. These experiments, published in 1774, suggested to him the conclusion, that the air of the atmosphere, or an elastic fluid contained in the air, is capable, in many instances, of being fixed and combined with metals; and that it enters into a similar combination in combustion. In subsequent experiments, he added to the evidence of these conclusions; he shewed more clearly that it is the oxygen of the atmospheric air that is absorbed in combustion; that it adds to the weight of the combustible body, this increase being equal to the weight of the oxygen that disappears; that it may be recovered from it either in a pure or combined state; that the result of this process is frequently the production of an acid; and that oxygen may be regarded as the principle of acidity *. Dr Black had, prior to these discoveries, established the important truth, that in the formation of vapour there is an absorption of caloric, which becomes latent; that when an elastic fluid is formed, a quantity of caloric is absorbed by it, without producing augmentation of temperature; and that, when it is condensed, caloric is given out. Lavoisier availed himself of these discoveries, and ascribed the heat and light produced in combustion to the escape of the combined caloric contained in the oxygen gas †.

Lavoisier was, after some time, aided in France by philosophers of distinguished talents, La Place, Guyton, Berthollet, and others; and the contest between the ancient and modern systems was warmly maintained. The original phlogistic doctrine could be no longer, indeed, defended, but various attempts were made to reconcile it with the modern discoveries. It could not be denied, that

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* Mémoires de l'Acad. des Sciences, 1775, 1776, 1777.
† Ibid. 1777, p. 420, 592.

in combustion oxygen gas is consumed ; but instead of admitting the simple conclusion, that this oxygen combines with the inflammable body, and that the phenomena of combustion are the result of this combination, it was attempted by various hypotheses to maintain the agency of a principle existing in inflammable bodies, and to preserve at least the language of Stahl.   There were thus established, as he remarked, " a number of doctrines, in which nothing of the original system remained but the name of phlogiston ; every one attached to this word a vague idea, which no one rigorously defined ; and they united, without perceiving it, in the same agent the most opposite and incompatible properties."

Of these hypotheses it is now unnecessary to take any notice.   Scheele's is distinguished by its boldness and ingenuity.   He supposed that the oxygen consumed in combustion, combines, not with the combustible body, but with the phlogiston it contains, and forms the heat and light which are evolved,—a supposition which accounted sufficiently for the necessity of oxygen to excite and support combustion, and for its consumption during the process, but which left unexplained the increase of weight which the combustible body gains.   Kirwan's was better adapted to the phenomena.   He advanced the supposition, that hydrogen is the principle of inflammability, or the common element contained in all inflammable bodies; the oxygen consumed in combustion combines, he supposed, with the hydrogen of the inflammable matter, forming with it a compound which remains united with that matter, and increases its weight.   Previous to the discovery of the composition of water, this hypothesis had some advantages, which were lost when that discovery was made. Less simple than the doctrine of Lavoisier, and supported by no proof, it was with much candour relinquished by its author ; and the discussion on the system of Stahl was closed.   Yet even still it has its influence, and it is a strik-

ing trait of prepossession to perceive in the development of new facts, and in the progress of the science, reference often made to an opinion advanced in its infancy, and which, to give it its highest praise, can be regarded only as an ingenious conjecture.

There are difficulties, too, attending the definition of combustion, which render it possible to oppose some objections to the theory of Lavoisier. But these are merely verbal disputes. In all cases of combustion, in the common acceptation of the term,—those cases in which a body, from the action of the air at a certain degree of heat, suffers a chemical change with the emission of light and elevation of temperature, the phenomena depend on its combination with oxygen. Not less unjust are the attempts which have been made to lessen the originality and the merit of Lavoisier's induction. The best proof of these is to be discovered in the implicit faith which was given to the established doctrines, and the support which, for a considerable period, they continued to receive.

I have now to state the facts by which the modern doctrine is established. Its first principle is, that combustion is the combination of oxygen with the combustible body. This is proved from the presence of oxygen being indispensable to that process; from the oxygen being consumed; from the increase of weight which the combustible body gains during combustion, corresponding to the weight of the oxygen that disappears; and from this oxygen being recoverable, either in a free or combined state, from the substance remaining when the combustion has ceased.

1st, Combustion does not go on without the presence of oxygen, and is more vivid where the oxygen is in a pure unmixed state. This is proved by numerous experiments. If a burning body be immersed in nitrogen, or any other gas, which does not contain oxygen. it is extinguished; or, if placed under a jar on the plate of the air-pump, on exhausting the air the combustion ceases, while,

in another jar of the same size, placed with its orifice in water, so as to cut off the communication of the air, it will continue burning for a longer time. Even in this last situation it will be in a certain time extinguished, that is, after the portion of oxygen contained in the atmospheric air in which it is placed is consumed. If, on the other hand, the combustible body be placed in oxygen gas, the combustion is much more vivid, and continues longer than in atmospheric air. There is one apparent exception, indeed, to the proposition. When an inflammable body is mixed with an equal weight of nitre and kindled, it burns with rapidity, though the atmospheric air be excluded ; and with some other saline substances, the effect is the same. But this is still a confirmation of the general result ; for these substances contain a large proportion of oxygen which they yield to the combustible body, and by which the combustion proceeds, independent of the presence of air.

2d, In every case of combustion, oxygen is consumed. This is proved by the facts, that a combustible body burns in a limited quantity of atmospheric air only for a certain time,—that the air is diminished in weight and bulk,— and that the combustion ceases when the diminution of volume amounts to about one-fifth part, that is, when the oxygen has all been absorbed. In oxygen gas, the diminution of volume is much greater, and, could the experiment be performed, combustion might be carried on until the whole of the oxygen, if it were pure, disappeared. This consumption of oxygen takes place in the burning of every kind of inflammable matter, though there are cases in which the diminution of volume in the air does not appear considerable. But this is owing to the substance, formed by the combination of the oxygen with the combustible body, being one which exists in the gaseous form, and which therefore remains mixed with the nitrogen of the atmosphere. When this is removed, the diminution is the same as in

any other case of combustion. In combustion in atmo-
spheric air, too, the process generally ceases before the
oxygen is entirely consumed. When the greater part of
it has combined with the inflammable body, the remaining
portion becomes so much diluted with the nitrogen gas,
that the combustion languishes, and at length so little oxy-
gen is in contact with the burning body that it is extin-
guished.

3d, In combustion, the combustible body always increa-
ses in weight, and the increase corresponds exactly to the
weight of the quantity of oxygen gas which disappears
during that process. Thus Lavoisier found that phos-
phorus, in burning, absorbs more than once and a half
its weight of oxygen gas, 45 grains of it consuming 69 of
oxygen; and that the weight of the substance produced,
during the combustion, " exactly equals the sum of the
weight of the phosphorus consumed, and oxygen absorb-
ed." He proved the same with regard to sulphur, char-
coal, and several of the metals : and indeed the proposi-
tion with respect to combustion is universal. There are
some cases, however, which, to superficial observation,
would appear to be exceptions; as in the combustion of
wood or coal, where there is only a small quantity of ashes
left after burning, not the hundredth part of the weight of
the fuel itself. But, in such cases, the principal product
of the combustion is a substance which assumes the ga-
seous form, and which therefore escapes unobserved : hence
if the combustion of such bodies be carried on in vessels
adapted to collect all the products, both volatile and fixed,
it will be found, that their weight is equal to the sum of
the weights of the inflammable body, and of the oxygen
consumed.

Lastly, the quantity of oxygen which is absorbed during
combustion, may be recovered from the compound that has
been formed; and the weight of this gas is equal to the
weight of the quantity which has disappeared during the

combustion. Thus, when quicksilver is heated in atmospheric air, it attracts its oxygen, and is converted into a red powder. If this powder be exposed to a stronger heat, it yields oxygen, and returns to the state of running quicksilver. The quantity of oxygen in this case is equal to the quantity which had been attracted by the metal from the air. In other cases, the oxygen cannot be expelled from the inflammable body by the operation of heat. But it may be separated by the superior attraction of a third substance; and the compound formed by the union of that substance with oxygen is then obtained. Thus the compound of iron with oxygen cannot be decomposed by heat. But if it be exposed to heat with a portion of charcoal, this substance exerts a more powerful attraction to the oxygen than the iron does; the iron is reduced to the metallic state, and the compound of charcoal with oxygen, carbonic acid, is disengaged. It being ascertained by previous experiments, how much oxygen is contained in a certain quantity of this compound, the quantity which was combined with the iron can be determined by the quantity of carbonic acid produced.

By these facts, then, Combustion is proved to be the combination of oxygen with the burning body : Combustibles are substances having an attraction to oxygen : And the substances formed by combustion are compounds of oxygen with these bodies.

Like other chemical combinations, this is much influenced by the degree of temperature. In general, the combination does not take place but at a high temperature, and therefore the application of heat is necessary to cause the combustion to commence. But after it is begun, as much caloric is extricated by the burning as is usually sufficient to keep up the necessary temperature, to cause it to proceed. This is different in different bodies. In some, as phosphorus, a very moderate heat is sufficient; in o-

thers, as sulphur or alkohol, a higher temperature, equal
to about 300°, is necessary; charcoal must be heated to
ignition, and the greater number of the metals require to
have their temperature raised far beyond this, to enable
them to combine with oxygen.

The effect of temperature, in exciting combustion, is to
be explained on the same principles as its effect in accele-
rating any chemical combination. Where the combustible
substance is a solid, the heat applied diminishes the cohe-
sive attraction, and so far favours the combination with
the oxygen, though this is no doubt counteracted to a cer-
tain extent, and therefore modified by the increased elas-
ticity communicated to the oxygen gas. Where it is in
the liquid state, the same effect will be produced; and at
the same time, in the greater number of cases the heat is
such as to volatilize the liquid; and its vapour, at the mo-
ment of its formation, or in the nascent state, must com-
bine with the oxygen with still more facility. In the case
of inflammable gases, the explanation is less obvious. Heat
favours their combustion; in other words, their combina-
tion with oxygen gas; and this is so far the case with re-
gard to the greater number of them, that a heat equal to
ignition is necessary to their combustion. Yet heat in-
creases elasticity; and if this state is an obstacle to chemi-
cal union, as it cannot be doubted is the case, it ought to
have in this case an opposite effect. I have already en-
deavoured to explain this, (vol. i, p. 106) by considering
heat as producing a local expansion in the mixed gas, and
thus giving rise to compression on the contiguous portion, so
as to cause approximation of the particles within the sphere
of mutual attraction. Grotthus gave the results of expe-
riments which are conformable to this view. He found,
that the facility with which an inflammable gas, mixed
with atmospheric air or oxygen is kindled, is considera-
bly dependent on the density, so that when the mixture is

rarefied by withdrawing pressure by means of the air-pump, it at length ceases to be capable of being inflamed; a mixture, for example, of oxygen and hydrogen gases ceases to inflame when expanded to sixteen times its original volume. Hence, as he remarked, at a great elevation in the atmosphere, inflammable bodies would lose the property of inflammability; while in a more dense atmosphere than that which exists at the surface of the earth, others might burn spontaneously, or with comparative facility. He farther found, that rarefaction by heat has the same effect as by diminished pressure *.

Sir H. Davy has, in some experiments, found the results to agree with the statement of Grotthus with regard to the latter, but not with regard to the former. On the contrary, rarefaction by heat appeared rather to facilitate the combustion; inflammable gases, mixed with oxygen, exploding even at a lower temperature if previously heated. Such mixtures too were inflamed when the heat was gradually raised to a certain point; and, on the other hand, condensation to $\frac{1}{7}$th of the original volume did not produce explosion. He inferred, therefore, that heat alone is the cause of the combination—" that at certain elevations of temperature, whether in rarefied or compressed atmospheres, explosion or combustion occurs, that is, bodies combine with the production of heat and light." The heat given out by the compression of gases is the real cause of the combustion which it produces; and, on the other hand, combustion is checked in a rarefied atmosphere only because sufficient heat is not produced to cause it to proceed. Sir H. Davy states a number of results according with these views, particularly that those combustible bodies which require *least* heat for their combustion, and those which produce *most* heat during burning,

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* Annales de Chimie, tom. lxxxii. Nicholson's Journal, vol. xxxv, p. 30.

are those which burn best in a rarefied atmosphere*. The difficulty, however, as I have already remarked, (vol. i, p. 99.) is to explain how heat should favour combination in elastic fluids, especially as it must affect their elasticity And that it operates by the compression it produces in consequence of this, is not perhaps invalidated by these results; for when the gaseous mixture is rarefied by heat, the elasticity is not diminished, and the re-action producing compression may take place to the same extent, as in the same mixture in a denser state at a lower temperature. That the effect is counteracted or prevented by rarefaction without elevation of temperature is admitted, which corresponds with the hypothesis. And that it should take place most readily in those gases which produce most heat in combining, and which require least for their combination, is precisely what is to be looked for.

Sir H. Davy found, that gases which explode from the heat of ignition, combine more slowly and without any apparent combustion at a lower temperature. This occurred in a mixture of oxygen and hydrogen gases, at a heat between that of boiling mercury and that approaching to the greatest that can be given without making glass luminous in the dark. And charcoal, he found, at a temperature a little above the boiling point of quicksilver, converted oxygen pretty rapidly into carbonic acid without any luminous appearance†.

On this fact is founded the striking result which he also discovered, of the ignition of a solid body, in a mixture of this kind in slow and imperceptible combustion. A wire of platina having been introduced into a mixture of coal gas and air in a state of inflammation, and more coal gas having been added, so as to extinguish the flame,

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* Researches on Flame, Philosophical Transactions, 1817, p. 45.

† Ibid. p. 56, &c.

that part of the platina which was hottest remained igni-
ted, and continued so for many minutes, though no flame
was to be perceived in the gas, even in a dark room. It was
evident, therefore, that the coal gas and the oxygen of the
air combined without flame, and yet produced heat enough
to preserve the wire ignited, and to keep up the slow com-
bustion. On plunging a fine platina wire heated into a
similar mixture of air and coal gas, it produced the same
combination, and as a consequence of it became ignited
and continued glowing for some time. The same result
was produced with mixtures of other inflammable gases.
Or the effect can be shewn in the vapour of ether, alkohol
or oil of turpentine mixed with air,—a coil of fine platina
wire being heated and suspended in a glass, in which a few
drops of ether, for example, have been allowed to fall. Pla-
tina and palladium were the only metals found to display
this result, a peculiarity arising from their low conducting
powers, and small capacities for heat, in consequence of
which they receive and retain a sufficient temperature to
keep up the combustion in the surrounding gas. An im-
portant practical application of this fact was made by Sir
H. Davy,—that of introducing a coil of platina over the
wick of the safety lamp used in coal mines, so that when
so much inflammable gas enters the lamp as to extin-
guish its flame, sufficient light is afforded from the ignited
wire to guide the miner, and on its removal into a purer at-
mosphere its heat is sufficient to rekindle the flame *. An-
other application of it is the singular arrangement of a
lamp without flame,—a coil of fine platina wire being sup-
ported over the wick of a spirit of wine lamp, and the flame
being blown out as soon as the platina is heated to red-
ness ; it continues ignited from the slow combustion of the
vapour, and by this state of ignition continues to support

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* Researches on Flame. Philosophical Transactions, 1817,
p. 77, &c.

the volatilization and silent inflammation, so that it remains luminous as long as the spirit is supplied [*].

On the effect of reduction of temperature below a certain point in diminishing the combustibility of mixtures of inflammable gases and air, depends the security given by a frame of net-work of metallic wire with small apertures, in preventing the communication of explosion from the carburetted hydrogen gas of coal mines, on which the safety lamp of Sir H. Davy is founded. The mixture of gas and air within the cage of net-work surrounding the lamp may be kindled; but in passing through the metallic tissue its temperature is so far reduced, that it is incapable of communicating explosion to the external gas [†].

Having established the cause of combustion, and illustrated the influence of the circumstances connected with it, it remains to explain the phenomena which are exhibited. The principal of these are the disengagement of light, and evolution of heat.

By the older chemists, it was supposed, conformable to popular opinion, that the heat proceeds from the inflammable body. It is an inference which must appear unquestionable while the nature of combustion is imperfectly understood. The burning matter appears luminous, and feels hot; no other agent appears to be concerned; it seems, therefore, the unavoidable conclusion, that it is from the combustible body that the heat and light are derived. But when the influence of the air in combustion is discovered,—when it is proved, that this process is the combination of the combustible matter with one of the constituent parts of the atmosphere, the oxygen gas, it is evident, that the former conclusion no longer necessarily follows; since it is equally possible, *a priori*, that they may be de-

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[*] Annals of Philosophy, vol. xi, p. 217, 305, 437.
[†] Philosophical Transactions, 1817, p. 68.

rived from the one, or the other, or from both ; and what-
ever may be their source, it is on the surface, where the
oxygen gas and the combustible body are in the act of com-
bination, that is, on the surface of the burning body, that
they must be evolved, and consequently it will appear lu-
minous, while the gas being invisible escapes observation.

The explanation of the production of heat in combus-
tion, is to be derived from the discoveries of Dr Black, Ir-
vine, and Crawford. Black had established the import-
ant truth, that bodies existing in the aërial form contain
at the same temperature more caloric than fluids or solids ;
and that when aëriform fluids are reduced to the fluid or
solid state, they render sensible a great portion of the la-
tent caloric they contain. When it was proved, therefore,
that in combustion an aërial body enters into combina-
tion, and passes generally into a denser state, it was an ob-
vious conclusion, that from its condensation the heat evol-
ved might be derived. Though approaching to the truth,
however, this explanation is not perfectly correct : it is
not the mere condensation of the oxygen gas that is the
source of the heat ; for the degree of it produced is not
proportioned to the degree of condensation ; and in differ-
ent cases, much heat is produced, where there is no con-
densation, the product of the combustion existing in the
aërial form.

Crawford considered this subject under a more just point
of view ; and it is to his application of a principle laid
down by Irvine, that we are indebted for that explanation
of the origin of the heat in combustion, which is most con-
formable to the laws caloric observes.

It had been demonstrated by Dr Black, that different
bodies have different capacities for caloric ; in other words,
contain at the same temperature different quantities of this
power. It had farther been shewn by Dr Irvine, that the
capacities of bodies are changed by chemical combination;
and he had assigned this as the cause of the heat which

occurs in some cases of chemical action. The state of che-
mical knowledge at that period did not allow him to ex-
tend the law to the production of heat in combustion. Dr
Crawford was enabled to make this application, and, in
the course of his researches, to establish it by experiment.
It had been established, that a quantity of oxygen gas is
consumed by every combustible body in burning; this oxy-
gen, according to the theory then generally maintained,
combining with the phlogiston of the combustible matter.
Crawford examined by experiment the capacity of oxygen
gas for caloric, the capacities of inflammable bodies, and
the capacities of the substances formed by their combus-
tion; and the result of these experiments proved, that oxy-
gen gas has a large capacity for caloric, or contains a large
quantity of it at a given temperature; that the capacities
of inflammable bodies are comparatively small; and, last-
ly, that the capacities of the substances formed by combus-
tion are superior to those of the inflammable bodies from
which they are formed, but inferior to the capacity of the
oxygen gas, and inferior also to the mean of the capacities
of this gas, and of the inflammable matter.— From these
facts, it followed, whatever the agency of the oxygen in
combustion might be, whether it enters into immediate
combination with the combustible body, or with any prin-
ciple of that body, that an elevation of temperature must
attend the process, and that the heat producing this must
be derived from the oxygen gas.

This theory was delivered by the author in the Medical
Society of Edinburgh in 1777, a period at least as early as
that at which any explanation was given of this phenome-
non by Lavoisier; and was published in 1779. Crawford
in his first experiments had fallen into considerable errors
in the estimation of the capacities. These he rectified,
and in 1788 published an enlarged edition of his work,—
a work which has been justly characterised, as containing
more of the philosophy of heat than any other. The prin-

ciple of the theory remains the same, and its admission sufficiently accounts for the evolution of heat in combination, though it has often been misunderstood. When a change of capacity happens, there must be an alteration of temperature; if the capacity is diminished, the temperature must be elevated, for the bodies suffering that diminution are incapable of containing the whole of the caloric which they before contained. In combustion, it is proved that such a diminution happens; in other words, the substance formed has a capacity inferior to the mean of the capacities of the oxygen gas and the combustible body; and as the capacity of the latter is inconsiderable, compared with that of the former, it is principally the caloric contained in the oxygen gas that must be evolved.

An example from Crawford's table of capacities will place this in a clear point of view. The capacity of oxygen gas is stated at 4.749, the capacity of charcoal at 263, or the oxygen contains a quantity of caloric expressed by the former number, proportioned to what is contained by the charcoal expressed by the latter number, at the same temperature, and in an equal weight. The capacity of carbonic acid, — the product of the combustion of charcoal, is 1.045,—inferior obviously to the mean of that of the oxygen gas and charcoal, but superior to that of the charcoal itself. The quantity of caloric, therefore, contained in the charcoal, is insufficient to supply the quantity which the carbonic acid produced from its burning will contain, and hence what is rendered sensible must be derived from the oxygen gas. This conclusion will become stronger, if we take into account the proportions in which these substances combine together, about $2\frac{1}{4}$ of oxygen being combined with 1 of charcoal, during its combustion. With this entering into the calculation, it can be shewn, as Crawford has stated it, that from the diminution of capacity which attends the burning of charcoal, as much caloric must be rendered sensible as if not dissipated, but applied to the

carbonic acid, the product of the combustion, would raise its temperature more than four times the excess of the heat of red-hot iron above the common temperature of the atmosphere *.

Similar examples might be taken from other inflammables. The only exception is hydrogen gas ; its capacity is even superior to that of oxygen, and therefore it must afford much of the caloric evolved in its burning.

Lavoisier had also advanced the opinion, that the heat in combustion is derived from the air, but he presented the theory in a much less distinct and less correct form. Assuming the distinction of free and combined caloric, and supposing that a large portion of caloric exists in oxygen gas in a combined state, he imagined it to be liberated in combustion by the oxygen combining with the combustible body †. This view of the subject rests on no just foundation. There is no reason to admit the existence of caloric in a state of chemical combination. The principle of Crawford's doctrine, that different bodies have different capacities for caloric, or contain in equal weights, and at equal temperatures, different quantities of this power, is, on the contrary, a simple expression of a fact. It is also proved by experiment, that in combustion the capacities of the bodies concerned are changed, and that the capacity of the product is inferior to the mean of the capacities of the oxygen gas and combustible body ; and from this it necessarily follows, that there must be elevation of temperature. Crawford's theory, then, is altogether independent of any speculation with regard to the nature of caloric, or its mode of existence. Whether we consider the temperature of bodies as depending on a peculiar principle, or as an effect produced by a force inherent in bodies, it must be admitted, that the quantity of this princi-

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* Crawford on Heat, p. 402.
† Mémoires de l'Acad. des Sciences, 1777, 1783.

ple or the intensity of this force may be augmented or diminished in them; that this augmentation or diminution may be rendered greater or less by communication with surrounding bodies which have a different temperature; that to produce a given temperature in equal quantities of different bodies, different quantities of this force or principle are necessary; and that, by chemical combination, a change in the relation or property whence this is required is produced. It is upon these general propositions, which are established by experiment, and independent of all hypothesis, that the evolution of caloric in combustion is explained.

More recent investigations, however, have been supposed to have thrown some doubt on this theory, by calling in question the accuracy of the experimental results with regard to the capacities of oxygen gas, and of combustible bodies on which it rests. It has been stated under this part of the subject of caloric, that Berard and Delaroche had assigned from experiment very different estimates from those given by Crawford. The capacity of oxygen gas they find to be inferior to that of the greater number of the gases, both combustible and products of combustion. It is inferior, for example, to that of carbonic acid, the capacity of the former estimated by volume being to that of the latter as 0.9765 to 1.2583. Now this precludes altogether the conclusion, that the heat in combustion is derived from the diminution of capacity in the oxygen gas. Nay, as oxygen gas is converted in the burning of charcoal into carbonic acid gas without any change of volume, it follows, on the doctrine of capacities, that there ought, from this enlargement of capacity, to be an absorption of heat, or production of cold, (for so large a quantity of caloric as would be necessary to give a different result cannot be supposed to exist in charcoal). Hence these chemists are disposed to explain the evolution of heat in combustion on the hypothesis of combined caloric. The weight due to these experiments, compared with those of

Crawford, has been already considered (vol. i, p. 388); there has appeared no reason to admit their superiority; on the contrary, the method by which they were executed is more complicated, and more liable to sources of fallacy than that of the other; the conclusions from them are at variance with very strict and extensive analogies; and the hypothesis of combined caloric rests on no legitimate induction, nor claims support even on any probable grounds.

There is another point of view under which this subject has been considered. A change in the electrical state of bodies is a cause of heat; and in particular where the positive and negative electrical states neutralize each other, it is often excited to a high degree of intensity, as is well displayed in the contact at the two extremities of the voltaic pile. This evolution of heat is not apparently connected with any of the known laws which regulate the distribution of this power. Electrical changes, there is reason to believe, are not unfrequently connected with chemical action; hence it has been supposed that they may prove in such cases a source of heat, independent of changes of capacity. And as combustion is a rapid and very intimate combination between substances having very energetic affinities, there is no case, it is conceived, more likely to occur, in which electric excitation shall operate, and give rise both to heat and light. This opinion, however, is vague. There is no proof that in these cases electrical changes do occur, or, if they did, that they give rise to any evolution of heat. That changes of temperature in chemical action are connected with changes of capacity is experimentally established; and it remains still to be clearly proved that there are cases in which these are not proportional to each other. If such should be demonstrated, the hypothesis of the excitation of heat by electro chemical action might be entitled to consideration; though even then the question would remain, from what source is this heat derived, and is it not dependent on momentary change

of capacity ? In the present state of our knowledge, how-
ever, we have neither any proof of the reality of its ope-
ration, nor of the necessity of its assumption as an hypo-
thesis.

It remains to explain the evolution of light in combus-
tion. While it was believed that light and caloric are the
same, or are modifications of the same principle, the same
origin was assigned to both. Stahl supposed both to be
extricated from the inflammable body : in the more mo-
dern theories of combustion, both have been derived from
the oxygen gas. But when this opinion of the identity of
light and caloric is not admitted, it becomes necessary to
inquire, whence the light evolved during combustion is
derived ?

In the system of Lavoisier it was supposed, that light is
a component part of oxygen gas, and that it is liberated
when the oxygen combines with the combustible body. In
support of this several arguments were advanced by Four-
croy and others, which are however altogether inconclu-
sive. Light, it was said, is more copiously extricated
when bodies burn in oxygen gas than when they burn in
atmospheric air. But this, it is obvious, is owing merely
to the greater rapidity of the combustion : a greater quan-
tity of the combustible body, as well as of the oxygen, is
consumed in a given time ; and therefore, whichever of
them the light proceeds from, a greater quantity must be
extricated. There are combustible bodies, it was said,
which do not burn with flame, except in oxygen gas,—a
repetition merely of the same argument; for in atmosphe-
ric air, the combustion of many bodies is so slow, that it
is not perceptible ; while in oxygen gas, being more rapid,
the light, whether it proceed from the oxygen or from the
inflammable body, is disengaged more suddenly, and is
therefore more apparent. To disengage oxygen from
burnt bodies, it is necessary, it was said, to communicate
light. But it remains to be proved, whether the light

added combines with the oxygen or the inflammable bo-
dy : it may as justly be supposed, *a priori*, that the light
exerts an attraction to the body with which the oxygen
was combined, as that it combines with the oxygen itself.
Lastly, There are burnt bodies, it was said, which lose their
oxygen on the contact of light alone, an argument to which
the same observation is applicable : we have no proof
whether the effect is produced by the light exerting an at-
traction to the inflammable body and combining with it,
or by attracting the oxygen, and with caloric forming oxy-
gen gas.

These facts, then, afford no presumption in favour of
the one hypothesis over the other ; neither is there any
thing more conclusive in support of the opinion, that the
light in combustion is derived from the oxygen gas.
Though there may be no decisive proof that it is disen-
gaged from the inflammable body, there are some facts in
favour of this opinion, at least if we admit the principle
that light is subjected to chemical affinities, and enters in-
to chemical combinations.

Thus, when the compound of oxygen with another bo-
dy is heated with an inflammable substance, it often hap-
pens that the oxygen is transferred from the former to the
latter, and there is a production of light : but this light
could not be derived from the oxygen ; for supposing it to
be a component part of oxygen gas, it must have been dis-
engaged during the first combination. Iron, zinc, anti-
mony, or arsenic, for example, burn with the emission of
light when heated in contact with oxide of mercury But
if light existed in oxygen gas, it would be liberated when
the oxygen combined with the mercury ; there is no rea-
son to believe that it would remain in the oxide, and the
light apparent must be derived from the metal with which
the oxide is heated. There are many cases of a similar
kind. When sulphur is burnt with oxygen, much light
is disengaged. In the product of this combustion, sul-

phuric acid, there is therefore no reason to believe that light exists. But when it is poured on certain inflammable bodies, such as the essential oils, these are oxidated by attracting its oxygen, and a vivid flame is suddenly produced. A number of deflagrations, in which oxygen is transferred from a body with which it is combined, to another inflammable substance, and in which there is a production of light, afford a similar proof.

Light too is disengaged in cases of chemical action, when there is no combination of oxygen. Thus when mixtures of sulphur with iron, zinc, or other metals, are exposed to heat, the sulphur and the metal combine, and at the moment of their combination an emission of light, in some of them vivid, and continuing a considerable time, takes place. In this case there is no oxygen present or necessary, the experiment succeeding, when the mixture is heated *in vacuo*, or in a tube containing nitrogen or hydrogen gas: The light, therefore, must be derived from one or both of these inflammables; and since there are thus proofs that light exists in inflammable bodies, and no proof equally conclusive that it is contained in oxygen gas, the inference is, that the light disengaged during combustion is derived from the combustible matter. At the same time the relations of light to other bodies are so peculiar, that nothing more than a probable conclusion can be drawn : nor is it with much precision that we can affirm any thing with regard to the combinations of light, or transfer to it the analogies of ponderable matter. There are other cases, indeed, in which light is rendered sensible as well as heat by chemical action, though there is no combination either of oxygen or of inflammable matter. A striking example of this is noticed by Chevreul. If either of the earths, barytes, or strontites, be introduced into muriatic acid gas, and heated gently, the gas is rapidly absorbed, and much heat, with a brilliant light, are disengaged, similar to vivid combustion. The phenomenon, as

he remarks, is one of those which prove that light is disengaged in combination, where the elements suffer great condensation with rapidity *. In other cases, even light is evolved from the separation of the elements of bodies, as well as from their combination, as in the example of the decomposition of the gas named euchlorine, at a moderate heat, or in that of the compound of nitrogen and chlorine, and of nitrogen and iodine. And these facts shew that we are very imperfectly acquainted with the chemical agencies of this principle, or the laws they observe.

The order in which the different prismatic rays of light are extricated in combustion appears to be considerably influenced by the temperature. Those bodies which burn at a low temperature, and do not raise their temperature high by their combustion, as ardent spirit or sulphur, emit the indigo and blue rays most copiously; charcoal, which requires a higher temperature, gives the red rays in greatest abundance: and in all cases where the combustion is rapid, and the heat intense, the rays are expelled in the proportion which constitutes white light. Mr Morgan supposed †, that this is owing to the different forces of attraction by which the different rays are retained by the inflammable body,—those which are retained by the weakest force, which, if this hypothesis be just, must be the indigo, being expelled at the lowest temperature; in proportion as the repulsive agency is augmented by the rise of temperature, the other rays will be thrown off, until it is raised so high that the attraction of all the rays is weakened, when the white light will appear. There is an objection to this, however, as Dr Price remarked, that the least refrangible rays are those supposed to be retained by the strongest attraction, while the property of inferior re-

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* Annales de Museum d'Histoire Naturelle, t. xviii, p. 407.
† Philosophical Transactions, vol. lxxv, p. 190.

frangibility seems to imply a less force of attraction be-
tween these rays and the bodies by which they are attract-
ed. The kinds of attraction in these cases might be sup-
posed to be different, though not perhaps with much pro-
bability.

Very different quantities of light are emitted by differ-
ent combustibles. In general the illumination is greatest
from those which are volatile, or which, while burning,
are in the state of vapour, as is exemplified in oil or wax
compared with charcoal, or in zinc among the metals: this
circumstance, however, is not essential, as is evident from
the bright light given by the combustion of phosphorus,
or by iron when burnt in oxygen gas. It will probably
be in a great measure dependent on the relative propor-
tions of light in different combustibles, and the force of
attraction with which they may retain it; and is no doubt
influenced by the rapidity of the combustion, or the quan-
tity of combustible matter burned in a given time. Sir
H. Davy has lately supposed [*], that the brightness of il-
lumination in flame depends in all cases principally on the
ignition or combustion of solid matter; hence in the in-
flammation of gases, from which there is no deposition of
such matter, the light is extremely weak, as in the example
of hydrogen: in the combustion of the compound inflam-
mable gases, such as carburetted hydrogen, the gas he sup-
poses is decomposed by the partial combustion in the in-
terior of the flame, and charcoal is deposited, the ignition
and combustion of which increases the illumination; and
conformable to this view, the introduction of solid matter
into a faint flame renders it more bright; and solid sub-
stances, if not volatilized during their combustion, give
much light. The heat is quite independent of the light

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[*] Researches on Flame, Journal of the Royal Institution,
vol. ii, p. 124.

in flame, and in general is most intense in that part of the flame where the light is weak.

The presence of incombustible matter often modifies the colour of the light emitted in combustion; the addition, for example, of different salts to alk hol, causes it to burn with different coloured flames. This might be ascribed to the influence of the incombustible matter modifying the temperature. Sir H. Davy has supposed, that the effect rather depends on the production and subsequent ignition of the inflammable matter which is the base of the saline substance; that the red colour, from the presence of the salts of lime, or the green colour, from that of boracic acid, depends on the combustion of calcium or boron, produced from decomposition, and present in the flame.

We have hitherto considered the simplest case of the combination of oxygen with other bodies. There are others more complicated, in which the oxygen is transferred from one body to another.

Deflagration is one of the most striking of these. If a mixture of nitre with an equal weight of sulphur, charcoal, or almost any other inflammable body, is thrown into a crucible heated to redness, a vivid combustion is instantly excited. The general explanation of this operation is sufficiently evident. Nitre is a salt formed by the union of nitric acid and potash; nitric acid consists of oxygen and nitrogen;—the solid salt, therefore, the nitre, contains a large portion of oxygen, and this oxygen is in such a weak state of combination, that it is expelled at a red heat. When the mixture of the nitre and of the inflammable body is thrown into the heated crucible, the oxygen of the former is disengaged, and is presented to the inflammable body; hence the vivid combustion that is excited. For the production of this, it is not even requisite to raise the temperature so high as that which would be necessary, if applied alone, to decompose the nitre, the affinity of the

inflammable body to the oxygen causing it to take place at a temperature somewhat lower. The nitrogen, the other constituent principle of the nitric acid, passes off in the state of gas ; and the potash with which the acid was united remains mixed, or united with the body formed by the combination of the oxygen and the inflammable substance. Any other salt containing the nitric acid has the same effect, as well as those salts which contain another acid, the hyper-oxymuriatic acid, all these yielding a large quantity of oxygen by the application of heat.

But though the general theory of this operation is obvious, the more minute explanation of its phenomena, particularly of the extrication of light and caloric which accompanies it, is attended with some difficulty. In combustion, the oxygen which combines with the combustible body, being in the gaseous form, may be supposed to afford the caloric which is set free, as substances in this form contain so large a quantity of caloric. But in deflagration, the oxygen transferred to the inflammable matter is in a concrete state, and can scarcely be supposed to afford so large a quantity of caloric, especially as the product of the deflagration is frequently gaseous.

To lessen this difficulty, it may be observed, that in the consumption of oxygen by deflagration, less caloric is evolved than in its consumption by combustion. This may be calculated from the experiments of Lavoisier and La Place *. Sixteen ounces of nitre contain about $6\frac{1}{2}$ ounces of oxygen. This quantity of nitre, deflagrated with charcoal melted in the calorimeter 12 lbs. of ice, which is in the proportion of $29\frac{1}{2}$ lbs. of ice melted by the consumption, by deflagration, of each pound of oxygen contained in nitre. But each pound of oxygen in the gaseous form, when burnt with charcoal, melts $37\frac{1}{2}$ lbs. of ice ; the quantity of caloric therefore disengaged during the consump-

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* Mémoires de l'Acad. des Sciences, 1780, p. 378—400.

tion of a given quantity of oxygen by deflagration, is considerably less than that disengaged by the consumption of the same quantity by combustion, the same combustible being employed.

In these cases, too, it is to be remarked, that the elements pass from combinations in which they are weakly united, to others more intimate and permanent; and hence a portion of caloric which may be supposed to exist with them in the former, may be expected to be expelled in the latter. It has even been ascertained, that when oxygen is combined with nitrogen, to form nitric acid, less heat is disengaged than in other combinations of oxygen. And again, when nitric acid is combined with potash, to form nitre, a very inconsiderable quantity is disengaged. It is certain, therefore, that a large quantity of the caloric contained in oxygen gas remains in the nitre. The case appears to be the same with those other salts which produce deflagration: and the principal difficulty is to determine, whether this large quantity of caloric, retained by oxygen in these combinations, is retained in them merely by their capacity being unusually large. Were it proved, as has been alleged, that the capacity of nitre for heat is not great, and that the united capacities of that salt and charcoal are inferior to the united capacities of the products of the deflagration of these substances, it would furnish the strongest argument against the opinion that caloric exists in bodies in proportion solely to their capacities. But the difficulty of the experiments must render the conclusions uncertain; at least this applies to any which have hitherto been made; and, in drawing such conclusions, it would be not less requisite to attend to the proportions of the substances concerned in the deflagration, which does not appear to have been done.

The origin of the light in deflagration must be the same as in combustion. If it is derived from the combustible body in the one, it may in the other; while, if it be a

constituent principle of oxygen gas, it may equally be derived from this source ; for when oxygen unites with nitrogen, no light is extricated, and therefore if oxygen gas do contain light, this light must remain combined with it, as it exists in nitric acid.

From the disengagement of the nitrogen gas, expelled from the decomposition of the nitre during deflagration, and the increase of its elasticity by the caloric liberated, a considerable expansive force is exerted, which is conspicuous when any resistance is opposed to the extrication of the gas. When the inflammable substance is one which, with oxygen, forms a compound that assumes the gaseous form, charcoal, for instance, which forms carbonic acid gas, another powerful elastic agent is introduced. It is on these circumstances that the great explosive force of gunpowder depends. This constitutes what in chemical language is termed Detonation. Deflagration is the rapid combination of concrete oxygen with an inflammable body, accompanied with the emission of light and caloric. Detonation is the same combination effected still more suddenly, and with an explosion of more or less force.

There are instances of detonation, in which there is no necessity for any arrangement producing resistance to the escape of the elastic products, but in which the elasticity of the gaseous products is such, that the mere resistance of the surrounding atmosphere is sufficient to give rise to a loud concussion or report. Detonation, too, is sometimes excited not only by heat, but by friction or percussion, either of which operates by approximating the particles of the inflammable body and the oxygen, whence their instantaneous combination, and the formation of an aëriform product. The mixtures most favourable for such detonations are those of salts, in which oxygen is retained by a weak affinity, and of an inflammable substance having a strong attraction to that oxygen, and forming with it an aërial product.

The last case of the general agency of oxygen to be explained is, that where it is transferred from one body to another, without the phenomena of combustion. Thus an acid often yields its oxygen to an inflammable body. In this case no great degree of heat is produced, owing partly to the oxygen, as it exists in the acid, having been deprived of much of its caloric, and partly to the product of the decomposition of the acid absorbing another portion of caloric. The process goes on, too, comparatively slowly, and therefore the caloric disengaged is less perceptible than if it were extricated in a shorter time. Neither does any disengagement of light attend this process, probably because it enters into a state of new combination ; if it leave the inflammable body, it will combine with the base of the acid, which returns to its original state. In some cases, however, part of the light is rendered sensible.

Water affords the oxygen it contains to some inflammable bodies, especially to some of the metals, and the phenomena are similar to those from the action of the acids, no light and little caloric being extricated. The process goes on slowly at a natural temperature, but is more rapid at a red heat, or at a low temperature when it is aided by the affinity of an acid.

The combination of oxygen with a body, whatever may be the phenomena attending it, is termed Oxidation or Oxygenation. These terms were objected to by Mr Chenevix, as the syllable *ate* is appropriated in chemical nomenclature to denote acids or compounds in which acids exist. Hence he proposed Oxidizement and Oxygenizement. The two terms, according to either nomenclature, are not quite synonymous, as is to be immediately explained.

The compounds of oxygen possess some common properties, and agree to a certain extent in the chemical agencies they exert. Hence they admit of some general observations.

When the compound of oxygen with a body has a sour taste, is capable of reddening the vegetable colours, and of combining with the alkalis, so as to neutralize the alkaline properties, it is named in chemical language an ACID. There are a number of Acids, or of substances possessing these properties, in which oxygen exists as a common principle. Hence this element has been considered as the principle of acidity, and from this indeed the name Oxygen has been derived.

Acidity, however, is not always the result of the combination of oxygen. The products of these combinations are often destitute of any acid property. It is convenient to have a term to denote this class of compounds, and accordingly in the modern nomenclature they are denominated Oxyds or OXIDES.

Oxides and Acids, then, are orders of compounds, under which are arranged the substances formed by the combination of oxygen with other bodies. Acids are distinguished by the possession of certain common properties just now enumerated. Oxides have scarcely any common qualities by which they are distinguished; the distinction being rather negative, or denoting that the compound has no acid power. The fixed alkalis and earths having been discovered to be compounds of oxygen, are to be regarded as oxides; and the most distinguishing property common to them, and likewise to all the metallic oxides, is that of neutralizing the properties of acids. But there are oxides to which this property does not belong. The word oxidation or oxidizement is used, in strict propriety, to denote that combination of oxygen where the resulting compound is not an acid, but an oxide. Oxygenation or oxygenizement is a more general term, expressing every combination of oxygen.

Many substances are capable only of oxidation. Thus the compounds which the metals form with oxygen are generally oxides; nor, with the exception of two or three

metals, by any addition of oxygen, ca nth ey be made to acquire acidity. Hydrogen unites with oxygen only in one proportion, and forms water, which is not acid.

There are other inflammable substances, which in combining with oxygen form in one proportion an oxide, and in another an acid. In general, the first degree of oxygenation forms an oxide, and this by combining with a larger proportion of oxygen forms an acid. Thus nitrogen united with nearly two parts of oxygen forms a substance, which, having no acid property, is an oxide of nitrogen, while, united with four parts of oxygen, it forms an acid compound. The case is the same with a number of other bodies. There are some, however, which form acids even in the first stage of oxygenation; at least their existence in the state of oxide is doubtful. But, in all those substances, which, by combining with oxygen in different proportions, produce both oxides and acids, the oxide is the product of the first stage of oxygenation, and the acid results from the addition of a larger proportion of oxygen. In some cases, the same substance in different degrees of oxygenation forms two acids different in their properties from each other; the one, from the larger proportion of oxygen, being usually the most energetic in its action.

The progress of discovery has led to some modifications of these views with regard to the relation of oxygen to acidity. Lavoisier had inferred, apparently from a very ample induction, in which a number of substances in combining with oxygen become acid, that it is exclusively the principle which communicates this chemical character. Berthollet had observed, however, that one acid at least, the prussic acid, contained no oxygen, and it was afterwards found that the compound of sulphur with hydrogen is unequivocally acid. Gay-Lussac, a few years ago, discovered that the base of prussic acid, (a compound of carbon and nitrogen, to which he has given the name of Cyanogen,) may be obtained in an insulated form, and that by its com-

bination with hydrogen the acid is produced. These facts seemed to prove, that hydrogen is an element which as well as oxygen confers acidity. From the more powerful acids a considerable quantity of water is obtained when they enter into other combinations, and this water seems essential to their existence in an insulated form, and to have an important influence in their properties. The result of some investigations led me to advance the opinion, that in these acids the elements of water, oxygen and hydrogen exist, not water itself, and that the results depend on the joint action of these elements. This view will fall to be illustrated more fully under the history of acids. At present it is sufficient to remark, that oxygen is not exclusively the principle of acidity, and that some of the preceding conclusions require to be modified, particularly that the same base with different proportions of oxygen forms different acids. In such cases hydrogen appears to enter into one of the combinations.

The alkalis and earths, which are two orders strictly connected, and having the same leading characters, contain oxygen as a common element, with the exception of one of them, ammonia, nitrogen and hydrogen being its constituents. The same views led me to conclude, that while in the other, alkalis, oxygen is the principle of alkalinity, in this substance hydrogen produces this result. The more powerful alkalis, too, were supposed to contain combined water. But conformable to this doctrine, the elements of water rather exist in their composition, and confer by their combined operation the alkaline quality. The illustration of this belongs to the general history of the alkalis.

BOOK II.

OF WATER AND ITS BASE.

Water, in the system of ancient philosophy, was considered as one of the elements from the union of which bodies are formed. The discovery of its composition, one of the most splendid and important of modern chemistry, was reluctantly admitted, and not until it appeared to be established by the most decisive evidence.

An inflammable elastic fluid had been known to be disengaged in certain chemical processes, particularly in the solution of metals in dilute sulphuric or muriatic acid. Mr Cavendish first examined its properties, and shewed that it is a distinct substance: he gave it the name of Inflammable Air. Macquer observed, that when this air is kindled in a glass vessel, some drops of a clear fluid are condensed, which appeared to him to be pure water. Lavoisier made a similar experiment, and by introducing lime-water, when the combustion had ceased, ascertained that no carbonic acid is produced; and in subsequent experiments he found that no other acid is formed. Priestley too fired mixtures of hydrogen with oxygen, and observed the deposition of water. It was at length concluded, nearly about the same time, by Watt and Cavendish, that water is a compound, formed from the combination of the base of this inflammable air with oxygen. The chemical history of oxygen having been already given, as a principle of atmospheric air, that of the other element

or base of water only remains to be delivered, prior to the history of the compound itself. In the modern nomenclature this base is denominated Hydrogen.

CHAP. I.

OF HYDROGEN.

THIS substance exists naturally in the aërial form. At an early period of chemical researches, its production in some processes, and its distinguishing property of inflammability were observed. Van Helmont had given it the name of Gas Igneum ; and it had attracted the attention of Boyle, Mayow and Hales. It is to Mr Cavendish that we are indebted for the first accurate account of its production and properties *. He gave it the name of Inflammable Air. From being considered as the base of water, it received, at the framing of the new nomenclature, the name of Hydrogen.

This gas is always obtained from the decomposition of water, as it cannot, from other substances in which it exists, be easily disengaged in perfect purity. The water is decomposed by some substance attracting its oxygen ; the hydrogen then passes into the elastic form. At natural temperatures this decomposition cannot be attained with rapidity by any single affinity : iron moistened with water decomposes it very slowly, and evolves hydrogen ; but at the temperature of ignition the decomposition is more rapid. If a coil of iron wire be put into an iron or coated

* Philosophical Transactions, vol. lvi, p. 141.

glass or earthen tube, placed across a furnace, and sur-
rounded with burning fuel so as to be brought to a red
heat, on distilling water through the tube, the vapour is
decomposed, the iron attracts its oxygen, and hydrogen
gas issues from the extremity of the tube.

By introducing the agency of an acid, water is decom-
posed rapidly by iron or zinc at natural temperatures, and
this affords a process more easy of execution.   One part
of zinc in small pieces is put into a retort, or into a bottle
with a bent tube adapted to it; two parts of sulphuric acid
previously diluted with five times its weight of water are
added; an effervescence immediately takes place, hydrogen
gas escapes, and may be collected in jars filled with water,
and placed on the shelf of the pneumatic trough.   Its dis-
engagement continues until the metal is dissolved.   Iron
containing generally a little carbon, which is dissolved by
the hydrogen, the gas it affords has been supposed to be
rather less pure than that afforded by zinc.   Muriatic
acid serves the same purpose as sulphuric acid, but must
be diluted with only three or four times its weight of wa-
ter.

In this experiment the hydrogen gas is derived from the
decomposition of the water, the oxygen of which is attract-
ed by the metal   That the acid suffers no decomposition,
is proved by the liquor at the end of the experiment being
capable of saturating as much of an alkali as the quantity
of acid employed would have done in a pure state.   The
agency of the acid in promoting the decomposition of the
water is somewhat difficult of explanation, and is such
certainly as could not have been inferred from any princi-
ple *à priori.*   It used to be explained on the doctrine of
Disposing Affinity, of which this indeed was considered
as a principal example.   The acid has an attraction to
oxide of iron, and by this attraction, it was supposed, it aids
so far the affinity exerted by the iron to the oxygen of the
water, that the affinity of the oxygen to the hydrogen is

overcome; the iron and oxygen combine, and the oxide of iron unites with the acid; an explanation liable to the obvious objection, that an affinity is supposed to operate to a substance before the substance actually exists. The effect, I have already remarked, is capable of being explained on the doctrine of resulting affinity. If the attraction exerted by sulphuric acid to oxide of iron be, as it probably is, the modified affinities of the acid to iron and oxygen, these may operate, though the oxide of iron is not actually formed; and though not singly of sufficient force to produce a combination of the acid, either with iron or with oxygen, may in union produce its combination with oxide of iron. If such forces exist, therefore, which from the considerations already pointed out under the review of the doctrines of attraction cannot be regarded as improbable, they may co-operate with the affinity of the iron to oxygen, and may thus overcome the single affinity of the oxygen to the hydrogen of the water.

Hydrogen gas is not always obtained by these processes perfectly pure. It is liable, in particular, to hold a little carbon in solution derived from that substance being not unfrequently contained in the metal. It may sometimes also, it appears, contain sulphur. To purify hydrogen gas, Mr Donovan passed a current of it produced from the action of a diluted acid on zinc or iron through a series of bottles,—the first containing ammonia, the second limewater, and the third common water; the ammonia acquired a fetid odour; muriatic acid added to it caused an exhalation of sulphuretted hydrogen; the lime water contained carbonate of lime, and when mixed with muriatic acid deposited a small quantity of sulphur. The smell of the gas thus purified was no longer the same, but similar to that of phosphorus; and it burned with a green instead of a blue flame. By passing it through nitrous acid, and from this through water, and a solution of sul-

phate of iron, it was rendered inodorous, and burnt with
so faint a light, that the flame was scarcely visible *.

Hydrogen is permanently elastic. When collected over
water, it has a peculiar smell, slightly fetid, which is not
so perceptible when it is collected over quicksilver, and
which is lost when the gas is exposed to substances which
powerfully attract humidity. It is not the only substance
in which water appears to develop odour. From Mr
Donovan's experiments, this odour may be inferred to de-
pend on foreign matter.

Hydrogen is the lightest of the gases, and the lightest
substance whose gravity can be ascertained by weighing.
Its specific gravity varies according to its state with re-
gard to humidity. When it has been transmitted through
water, or has been exposed to it, it is about ten times
lighter than atmospheric air; when it has been received
over quicksilver, and exposed to any substance which frees
it from aqueous vapour, it is nearly thirteen times lighter:
From its great levity its precise specific gravity is estimated
with more difficulty than that of any other gas. Accord-
ing to Biot and Arrago, atmospheric air being 1.00000,
pure hydrogen gas is 0.07321. Dr Prout has stated it
somewhat lower. It is liable, he remarks, to be over-rated,
from the difficulty of obtaining it pure, and of abstracting
aqueous vapour from it entirely. It may therefore be bet-
ter determined, by calculation, from the specific gravity of
a gaseous compound in which it exists in a known pro-
portion, and with a certain condensation. In ammonia
3 volumes of it are combined with 1 of nitrogen, con-
densed into 2 volumes; and calculating from this, its spe-
cific gravity is 0.0634; this is exactly 16 times lighter
than oxygen gas. 100 cubic inches, according to this esti-
mate, weigh 2.118 gr. at 60° of temperature, and 30 of
barometrical pressure. The weight from direct experiment

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* Philosophical Magazine, vol. xlviii, p. 138.

is 2.23. It is from the levity of this gas that it has been applied to the construction of balloons, a varnished silk or linen bag filled with it, having a specific gravity so much less than atmospheric air, as to rise iu the atmosphere and elevate an additional weight.

The chemical property by which hydrogen gas is most eminently distinguished, is its inflammability. When an ignited body is approached to it in contact with the atmosphere, it kindles and continues to burn while the air is admitted ; if previously mixed with twice its volume of atmospheric air, on approaching a burning body to the mixture, or sending an electric spark through it, it inflames with detonation ; and when it is mixed with oxygen gas, the detonation is more violent.

When a current of hydrogen gas from a small aperture is made to burn, on bringing a wide tube over the flame, a singular phenomenon, accidentally observed by Dr Higgins, is produced,—that of sounds of various tones, which vary in acuteness and strength, according to the width, the length of the tube, and the kind of substance of which it is formed,—owing apparently to the vibrations excited in the matter of the tube by the rapid expansion and condensation of the watery vapour near and around the flame, and which, regulated and equalized by regular reflections from the sides of the tube, constitute a clear sound.

From its inflammability hydrogen gas has been applied to the purpose of endiometry. A given measure of it is put into a tube, Fig. 50. with a quantity of the air designed to be submitted to trial, and is inflamed by the electric spark, the diminution of volume indicating the quantity of oxygen. This is the method of Volta : 100 measures of oxygen require 200 measures of hydrogen for saturation ; about 42 measures of hydrogen are, therefore, sufficient to saturate the oxygen contained in 100 measures of atmospheric air, but it is proper to use an excess of hydrogen, as otherwise part of the oxygen is liable to

escape combination.   Equal measures of the two airs are
often employed ; this, however, is an unnecessary excess
of hydrogen ; 50 measures of hydrogen to 100 of atmos-
pheric air is a better proportion ; the mixture is intro-
duced into the detonating tube, and is inflamed by the e-
lectric spark ; the diminution of volume is observed accu-
rately, and the third part of this is the volume of oxygen
in the air submitted to trial.   Thus, employing the above
proportions, the 150 measures will be reduced by the de-
tonation to 87 measures : the diminution, therefore, is 63,
and the third of this gives 21, as the proportion of oxygen
in atmospheric air.   To obviate the risk of any part of the
air being driven out of the tube by the explosion, and to
prevent the expulsion of air from the water if the tube
were closed and a vacuum formed from the condensation,
the modification of the instrument, Fig. 51., (described
vol. i, p. 587.) may be employed.

This method is simple and expeditious, and it has the
advantage, from the bulk of the mixture, and the great di-
minution of volume from the consumption of a given quan-
tity of oxygen, of being more delicate than any other, each
measure of oxygen consumed giving a diminution of three
measures, so that any error of observation, or error from the
graduation of the scale, must be extremely trivial.   It also
requires no corrections for variations of temperature or at-
mospheric pressure.   It has been supposed liable to a source
of error from the hydrogen holding sometimes in solution
a little carbon, derived probably from the metal by which
it is procured, which will, in the detonation, give rise to
the formation of a little carbonic acid; any error from this,
however, must be extremely trivial ; the degree of impu-
rity, when zinc is employed in the preparation of the hy-
drogen, being so inconsiderable.   It appears too from
Saussure's observations, that when an excess of hydrogen is
used, the carbon remains dissolved in it without combin-
ing with the oxygen : farther, any minute portion of car-

bonic acid that may be formed will be absorbed by the water, and add nothing to the residual gas; and the difference in the proportion in which carbon combines with oxygen, compared with that in which hydrogen combines with oxygen, is such as on so small a quantity can give rise to no perceptible error. Saussure has stated, that a little of the nitrogen combines with the oxygen, when there is a deficiency in the proportion of hydrogen employed, forming nitric acid, and, on the other hand, when there is an excess of hydrogen, a little of the nitrogen combines both with hydrogen and oxygen, forming nitric acid and ammonia, and that from this, the indications given by the eudiometer of Volta, vary according to the proportions of the airs [*]. Another source of error is, that the pressure from the detonation forces out a little air from the water over which the experiment is made, which adds to the volume of the residual air [†]. But this appears to be of importance only when the method is employed to ascertain the purity of oxygen, and according to Berthollet is best obviated by employing such proportions of the gases, that there shall be a pretty large residuum. If the proportions are such that the two gases are nearly consumed, or the residuum is not more than one-sixth of the original mixture, the evolution of air from the water is a source of error; when it amounts to one-fourth, its influence is scarcely perceptible, and when equal to one-half, it may be altogether neglected [‡]. The other errors appear in practice to be very trivial. The method agrees very nearly in its results with the most accurate eudiometrical processes, and Humboldt and Gay-Lussac, in an elaborate memoir, have shewn, that they do not vary from

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[*] Nicholson's Journal, vol. xxvi, p. 74.

[†] Ibid. vol. xviii, p. 128.

[‡] Mémoires d'Arcueil, t. ii, p. 288.

each other, when the necessary precautions are attended to *.

Detonation with hydrogen affords the best method of determining the purity of oxygen gas, and also the proportion of it in any gas that contains it in considerable quantity in a state of mixture. It also affords the best mode of discovering the presence of a small portion of hydrogen itself in atmospheric air or oxygen gas, a given quantity of hydrogen gas being added to the mixture, so as to render it capable of being inflamed by the electric spark, and the diminution of volume which exceeds that which would be produced from the condensation of the quantity of hydrogen added, indicating the proportion of hydrogen which the air had contained.

Hydrogen gas is incapable of supporting the combustion of other inflammables. If a burning body be immersed in it, it is extinguished.

This gas is incapable of supporting animal life by respiration ; an animal immersed in it is soon killed. It does not, however, appear to be so positively deleterious as the other noxious gases. Scheele was able to breathe it for 20 inspirations †. Fontana shewed, what Scheele indeed had observed, that if the lungs were previously emptied as much as possible of atmospheric air, by a forcible expiration, it cannot be breathed so long, though still it did not appear to him to be positively deleterious, like some of the unrespirable gases ‡. Rosier, even after expelling the air from the lungs, breathed hydrogen gas for several respirations ; and Davy, in one experiment, after a complete exhaustion of the lungs, breathed it for half a minute, and in a subsequent experiment, with the same preparation, for near a

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* Journal de Physique, tom. lx, p. 129.
† Treatise on Air and Fire, p. 160.
‡ Opuscules Physiques, p. 2.

minute. The first six or seven inspirations produced no sensations whatever; in half a minute, a sense of oppression was felt at the breast, which increased until the pain of suffocation interrupted the experiment *. Hydrogen, therefore, is incapable of supporting life; it appears only to prove fatal, not by a positively noxious quality, but by excluding atmospheric air, the due supply of which by respiration is indispensable to life. Blood exposed to it acquires a deep black colour, and the gas suffers a diminution of volume.

Hydrogen is not, as several of the other gases are, noxious to vegetable life; at the same time it appears to contribute little to the nourishment of plants, Dr Priestley having found that it still continued inflammable after a growing vegetable had been confined in it for several months. It can apparently supply, to a certain extent, the place of light in supporting vegetation. Van Humboldt observed that some cryptogamic plants in mines, and of course secluded from light, were not pale, but of a green colour, similar to that which they would have had from growing under exposure to the light of day; and he concluded with probability, that the agency of light had in this case been supplied by the hydrogen gas which is often extricated in such situations.

Hydrogen gas is so sparingly soluble in water, that agitated with it, it suffers no perceptible diminution of volume. When the water has been freed from atmospheric air, Henry found that 100 cubic inches take up 1.5 of the gas under a common atmospheric pressure; under increased pressure, a larger quantity, equal to one-third of the volume of the water, is absorbed.

The affinities of hydrogen are principally exerted to inflammable bodies. It unites with sulphur, phosphorus and carbon, and forms gaseous compounds; it is capable

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* Chemical Researches, p. 400, 466.

of dissolving even some of the metals, particularly tellurium and arsenic. United with nitrogen, it forms one of the alkalis, ammonia, and with oxygen, water. It is also a constituent principle of the greater number of the vegetable and animal products. Its binary compounds are named Hydrurets.

Hydrogen in some of its combinations appears to communicate the property of acidity. Its compound with sulphur is distinctly acid; and in combining with the compound radical cyanogen, it forms prussic acid. In other powerful acids it exists along with oxygen; and a higher degree of acidity, it has been already remarked, is acquired from the joint action of these two elements, than from that of either alone. The same law appears to apply to the constitution of the alkalies; and in one of them, ammonia, hydrogen alone seems to communicate the alkaline properties. These agencies of it are to be afterwards illustrated. The peculiarity of it may be remarked,—that of all the bodies which combine with oxygen, it alone forms a compound having neither acid nor alkaline properties. This is probably to be explained on the principle, that oxygen and hydrogen are elements, each of which, in acting on inflammables or metals, communicate acidity or alkalinity. A radical therefore is necessary to admit of either of these chemical qualities being developed by their operation; and hence in their mutual action it is not produced.

Hydrogen gas may be regarded as a product of some natural operations, not indeed perfectly pure, but forming the predominating ingredient in certain inflammable gases, generally in combination with carbon. In this state it is sometimes collected in mines, being known to the miners by the name of Fire Damp, and is often the cause of accidents, from exploding on the approach of an ignited body. It is also extricated from stagnant water, and from marshy situations, from the slow decomposition of vege-

table and animal substances, holding dissolved not only carbon, but probably other substances, and forming, as has been supposed with some probability, gases which render the air of such places unhealthy. From its levity it has been imagined that the quantity of it produced at the surface of the earth will rise and occupy the higher regions of the atmosphere; and on its presence some of the phenomena of meteorology, particularly the sudden appearance of some fiery meteors, have been supposed to depend. There is no reason to believe, however, that hydrogen would ascend in the atmosphere and remain distinct: if added to atmospheric air, it would observe the usual law of the mutual weak action of aërial fluids, and be diffused through it; and even if it were accumulated in the higher regions of the atmosphere, its rarity would be such that it could not be inflamed.

The recent discoveries in chemistry suggested some hypothetical views with regard to the nature of hydrogen. Ammonia, one of the alkalis, is a compound of hydrogen and nitrogen. Berzelius and Pontin, operating on this substance, discovered, that when quicksilver, negatively electrified in the galvanic circuit, is in contact with a solution of ammonia, it increases in volume, acquires consistence, and, when it has increased to four or five times its original dimensions, becomes a soft solid. These are changes analogous to what would be produced in it by the addition of metallic matter; and hence they led to the conjecture, that one or both of the elements of the ammonia is metallic: hydrogen being highly inflammable, a property which belongs to metals, it was considered as being more probably the metallic base of the ammonia; and it was conjectured to be either a metal in the gaseous form, or a metal in some state of combination, probably oxidated. It has sometimes also been conjectured that hydrogen is a common principle of inflammability, existing in all inflammables and metals. This is, however, en-

tirely hypothetical; and the other speculations have not
received any confirmation from the progress of discovery.
The nature of the amalgam from ammonia remains unde-
termined; but it appears from the experiments of Gay-
Lussac and Thenard, to be probably a compound of ammo-
nia and hydrogen with quicksilver; and these substances
may produce the change which takes place in the proper-
ties of the quicksilver, though they communicate nothing
truly metallic. The properties of water, the compound of
hydrogen and oxygen, are so totally different from those
of metallic oxides, as to render improbable the conjecture
that hydrogen is a metal in the aërial form; and a similar
improbability attaches to the supposition from the small-
ness of the equivalent quantity in which hydrogen enters
into chemical combinations. In this last relation it exceeds
all other bodies, being the one the combining weight of
which is smallest; and from this, as well as from its low
specific gravity, it appears to form the commencement of
the series of ponderable substances, and to approach nigh-
est to the elementary state. From recent investigations,
its chemical agencies, too, appear to be more important
than had been before supposed; in this respect it stands
nearly in the same rank with oxygen; and an immense
series of chemical changes are connected with the action
of these elements.

CHAP. II.

OF WATER.

WATER, it has been stated, is produced when hydrogen is made to burn; and when oxygen is abstracted from water by substances having a strong affinity to that element, hydrogen is evolved, and assumes the elastic form. The conclusion appears, therefore, necessarily to follow, that water is a compound of these two gases. This conclusion was drawn nearly at the same time by Watt and by Cavendish; the memoirs of these philosophers on this subject having been published in the same volume (the 74th) of the Philosophical Transactions.

It was suggested to Mr Watt by some experiments made by Priestley, in which metallic oxides were reduced to the metallic state, by being heated in hydrogen gas; and others in which, when mixtures of hydrogen and oxygen gases were fired in close vessels, moisture was deposited, without any other sensible product; and this moisture, when absorbed by a sponge, was found equal to the weight of the gases employed. Regarding hydrogen, in conformity to an hypothesis at that time maintained, as the principle of inflammability, or phlogiston, he inferred, that since water is the only sensible product of the combination of the two gases, (besides the heat and light which are disengaged,) it is probably a compound of phlogiston and oxygen.

This was established, on evidence still more decisive, by

Mr Cavendish, whose attention had been likewise directed to this subject by Priestley's experiments on the burning of hydrogen. To ascertain the nature of the product, he burnt large quantities of this gas. In one experiment, 500,000 grain measures of hydrogen gas were burnt slowly in common air, and the current of air was made to pass through a cylinder of glass, in order to deposite the dew. Upwards of 135 grains of water were condensed in the cylinder, which had no taste nor smell, which left no sensible sediment when evaporated to dryness, nor gave any smell during the evaporation ; which, in short, seemed to be pure water. This being the only sensible product of the combination of hydrogen and oxygen, Mr Cavendish considered it as a compound, formed by their union.

The experiment of burning hydrogen gas was made the same year by Lavoisier, who had been informed by Dr Blagden of the experiment having been made by Mr Cavendish, of the result, and the conclusion drawn from it; and so far was he from having conceived an idea of this discovery, that, as Mr Cavendish has stated, " until he was prevailed upon to repeat the experiment himself, he found some difficulty in believing, that nearly the whole of the two airs could be converted into water *." He obtained nearly five drachms of water perfectly pure †. Monge made a similar experiment, and found that the quantity of water procured is equal to the quantity of the gases which disappear; and in subsequent experiments which Lavoisier made, assisted by Meusnier, he endeavoured to determine the proportions in which they combine. They also established the composition of water by decomposing it, by substances which attract its oxygen, as well as by a reference to the experiments of Priestley,

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* Philosophical Transactions, vol. lxxiv, p. 134.
† Mémoires de l'Acad. des Sciences, 1781, p. 473.

in which some of the metallic oxides were reduced by hydrogen gas, assisted by heat [*].

The discovery of the composition of water, besides its intrinsic importance, derived at the time it was made an adventitious importance from its relation to the explanations of the antiphlogistic doctrine, which were at that time warmly contested. It was known, that during the solution of metals in certain acids hydrogen gas is disengaged; and it had been observed by Priestley, that when several of the metallic oxides are heated with this gas, they are reduced to the metallic state, without any oxygen being afforded by this reduction, the hydrogen at the same time disappearing. These facts were inexplicable on the antiphlogistic system; it could give no account of the origin of the hydrogen in the one case, nor of its disappearance in the other, and they were therefore urged with much force by the opponents of this system, as a proof of the opinion which they began to adopt, that hydrogen is the phlogistic principle. The discovery of the composition of water solved, however, these difficulties; hence its reality was for a time disputed, and there were certain ambiguous circumstances in the experiments that afforded room for doubt.

The principal circumstance of this kind was the apparent production of an acid during the combustion of the hydrogen; the water condensed being frequently sensibly acid. It was concluded, that this acid is the real product of the combustion, and that the water collected is the portion that had been held by the gases in solution. By farther investigation, however, this uncertainty was removed; and the circumstances from which the production of acid arises were pointed out by Cavendish, and their operation explained [†].

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[*] Mémoires de l'Acad. des Sciences, 1781, p. 478.
[†] Philosophical Transactions, vol. lxxiv, p. 131, &c.

The acid formed was in general the nitric. Now, this acid is a compound of oxygen and nitrogen ; and as it is difficult to procure oxygen gas free from a small admixture of nitrogen, the latter obviously might furnish by combination with oxygen the small quantity of nitric acid occasionally found.

It was accordingly discovered, that this production of nitric acid might be regulated at pleasure. Nitrogen does not combine with oxygen so readily as hydrogen does ; if, therefore, the combustion was carried on slowly, water might be formed, without any sensible acidity, even though nitrogen were present. This was the case in Mr Cavendish's experiment, in which atmospheric air was used. Nay, what appears at first view singular, and contrary to the cause assigned, water formed by burning hydrogen in atmospheric air is generally free from acidity ; while it is acid, when formed by burning hydrogen in oxygen ; the reason of which is, that in atmospheric air, the temperature produced by the combustion is not sufficiently high to cause the combination of the oxygen and nitrogen, while in oxygen gas, the heat produced at the point where the combustion proceeds is more intense, and the nitrogen present is brought into combination. The production of acid was also found to depend on the proportion of the gases. If no more oxygen was present than what is necessary to saturate the hydrogen, the water formed had no acidity ; but if the oxygen were in larger quantity, a portion of acid was formed ;—the excess of oxygen combining with the small quantity of nitrogen intermixed. According to the observations of T. Saussure, there is even a formation of nitric acid when an excess of hydrogen is present, but the acidity is not apparent, because there is at the same time a production of ammonia, by the union of part of the hydrogen and nitrogen, and this neutralizes the acid *.

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* Nicholson's Journal, vol. xxvi, p. 176.

In some cases the acid was found to be not the nitric, but the carbonic : its origin is to be traced to the small quantity of carbon held in solution by the hydrogen gas derived from the metals by which it is prepared, and which by combination with oxygen forms carbonic acid. From Mr Donovan's experiments, too, it appears that hydrogen sometimes holds a little sulphur combined with it, which will yield a minute portion of sulphuric acid; and he accordingly detected this acid in the water formed from its combustion, if the gas had not previously stood for some time over water, by which the minute portion of sulphuretted hydrogen would be absorbed.

When care is taken to obtain the gases free from these impurities, or, by the manner of conducting the experiment, to prevent their combination with the oxygen during the combustion, the water is obtained perfectly free from acidity, or from any other impregnation, and its weight is equal to the weight of the oxygen and hydrogen combined. This latter fact has been established by very accurate experiments on a large scale,—experiments which appear to obviate every objection, and leave no doubt as to the composition of water.

An experiment of this kind, in which a large quantity of the gases were combined with an accurate attention to the proportions, was made by Monge, in 1783. By repeated explosions, in a close vessel, of a mixture of the two gases duely proportioned, 145 pints of hydrogen and 74 pints of oxygen were consumed; weighing, according to his estimate, 3 ounces 6 gros 27.56 grains. The product of water was 3 ounces 2 gros 45.1 grains. There was a residuum of air in the vessel, which weighed 2 gros 27.91 grains; on the whole quantity, therefore, there was a *deficit* of 1 gros 26.55 grains, which Monge accounted for from the imperfect manner in which he had made allowance for variations of barometrical pressure in estimating the volumes of the gases consumed in the progress of the experiment,

and from no allowance having been made for changes of temperature in the vessels containing the gases contiguous to the balloon in which the explosions were made. The water obtained was slightly acid *.

La Fevre de Gineau, in 1788, made the experiment on a large scale. The volume of oxygen gas employed amounted to 35085.1 cubic inches, its weight to 254 gros 10.5 grains; the volume of hydrogen gas was 74967.4 cubic inches, its weight 66 gros 4.3 grains. The whole, therefore, weighed 320 gros 14.8 grains; but the gases being not perfectly pure, there remained uncombined a quantity of air, consisting of oxygen, nitrogen, and carbonic acid, which weighed 39 gros 23 grains. The real quantity combined, therefore, was 280 gros 63.8 grains, or 2 pounds 3 ounces 63.8 grains; the water produced weighed 2 pounds 3 ounces 33 grains. There was thus, on so large a quantity, a deficit only of 30.8 grains; and, considering the difficulty of estimating with perfect accuracy the weight of the gases, this may be regarded as a near approximation. The water was sensibly acid from the presence of nitric acid †.

But the most accurate experiment made by the French Chemists, was one by Fourcroy, Vauquelin and Seguin, in which every attention was paid to obviate sources of error. The oxygen was procured from the decomposition of oxymuriate of potash by heat, the hydrogen gas from zinc, and sulphuric acid diluted with water. The combustion was carried on as slowly as possible, that any nitrogen present might not be combined with oxygen. The experiment continued 185 hours without interruption. The quantity of hydrogen employed amounted to 25980.563 cubic inches; of oxygen, 13475.198. There remained a quantity of gas, which amounted to 987 cubic inches, and

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* Mémoires de l'Acad. des Sciences, 1788, p. 78.
† Journal de Physique, tom. xxxiii, p. 460.

which on examination was found to consist of nitrogen gas 467, carbonic acid gas 39, oxygen gas 465, and hydrogen gas 16. After making due correction for the quantity of hydrogen which remained after the combustion, and for the quantity of carbon contained in the hydrogen gas that was consumed, and which had formed carbonic acid, and after making a similar correction for the quantity of oxygen which remained, and for the quantity of it that had been spent in the formation of carbonic acid, it appeared that there had entered into combination, so as to form water,

	Cubic inches.		Grains.
Hydrogen gas,	25963.563,	weighing	1039.358
Oxygen gas,	12570.942,	————	6209.869
The total weight of gases, therefore, was			7249.227
The quantity of water produced was			7245
The deficit, therefore, amounted only to			4.227

The water shewed no sign of acidity; with nitrate of lime, it formed no precipitation, nor cloudiness; its specific gravity was to that of distilled water as 18671 to 18670 [*].

The last experiment which may be noticed, is one made by Dr Higgins, before a philosophical society in London, with an apparatus more simple, but sufficient to give an accurate result: 416.5 grains of oxygen gas, and 72.5 grains of hydrogen gas were consumed, the weight of both being 489. The water produced, which was perfectly pure and free from acidity, weighed 487 grains [†].

These experiments appear sufficient to establish the conclusion, that water is a compound of oxygen and hydrogen. In some of them it was obtained perfectly pure; was the only sensible product; and corresponded in weight, as exactly as could be expected from experiments in which gases are weighed, to the weight of the hydrogen and oxy-

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[*] Mémoires de l'Acad. des Sciences, 1790, p. 485.
[†] Minutes of a Philosophical Society, p. 194.

gen which disappeared. This coincidence of weight, and absence of all other sensible product, are sufficient to refute the opinion at one time maintained, that the water is merely that which pre-existed in solution in the gases deposited during their combination.

These experiments by synthesis have been likewise confirmed by analysis. This was effected by Lavoisier and Meusnier. They passed water in vapour through an iron tube, red hot, or through a tube of copper with a spiral piece of iron inclosed; hydrogen gas was disengaged in considerable quantity, and the iron increased in weight, and had lost nearly its magnetic property *. The experiment was afterwards made by Le Fevre de Gineau, so as to prove that the quantity of hydrogen collected, added to the increase of weight which the iron gains, is equal to the quantity of water that disappears, or at least as nearly so as the nature of the experiment will permit the estimate to be made with accuracy †. According to a subsequent statement by Lavoisier, soft iron-wire rolled spirally being placed within a coated glass tube raised to a red heat, on transmitting through it the vapour of water from a retort, when 100 grains of this water disappear, the iron in the tube increases in weight, 85 grains, by combination with the oxygen of the water, and 416 cubic inches of hydrogen gas, weighing 15 grains, are obtained ‡.

Even at a low temperature, some of the metals, especially iron and zinc, decompose water with rapidity when their action is aided by that of an acid. This is the common process for obtaining hydrogen gas, sulphuric acid being diluted with 6 or 7 times, muriatic acid with 4 or 5 times, its weight of water, and poured on zinc in small pieces, or on iron-filings or wire. That the acid merely promotes

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* Mémoires de l'Acad. 1781, p. 269.
† Journal de Physique, tom. xxxiii, p. 464.
‡ Elements of Chemistry, p. 140.

the decomposition of the water by its agency, and does not afford hydrogen, is proved by the fact that it remains in the fluid undecomposed, being able to saturate just as much of an alkali as it would have done in its pure state ; and that the metal receives oxygen, is proved by its being found in an oxidated state. This was ascertained with much accuracy by Dr Fordyce ; a given weight, 1000 grains of diluted sulphuric acid, being saturated with a solution of potash, and the quantity of sulphate of potash formed being obtained by evaporation: it amounted to 978 grains. The same quantity of the same acid was employed to dissolve zinc, and, on adding to the solution, solution of potash, so as to precipitate the metallic oxide, the liquid, together with the quantity of water employed to wash the precipitate, afforded by evaporation a solid substance, which, on re-dissolving it in water to separate a little adhering oxide, and again evaporating, afforded $976\frac{1}{10}$ grains of sulphate of potash ; a difference so inconsiderable as obviously to have arisen from the accidental loss which must attend such experiments. 164 grains of zinc had been dissolved ; the oxide, after being dried by a red heat, weighed 220 grains ; the metal therefore had gained weight equal to 56 grains, which, from the preceding experiment, must have been derived from the oxygen of the water. And, by a subsequent experiment, Dr Fordyce shewed that a quantity of water equivalent to this disappeared during the solution [*].

From the synthesis and analysis of water, by the experiments now described, the proportions of its constituent principles have been determined. They vary a little as inferred from different experiments.

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[*] Philosophical Transactions, 1792, p. 374.

	Hydrogen.	Oxygen.
Lavoisier stated the proportions at	15	85
Lavoisier and Meusnier, at -	13.1	86.9
Le Fevre de Gineau, from the ana- lysis of water, at - -	15.7364	84.2636
From the formation of water, -	15.2	84.8
According to Fourcroy, Vauquelin and Seguin, they are - -	14.338	85.662

Gay-Lussac and Humboldt, at a subsequent period [*], justly remarked, that the proportions of hydrogen and oxygen gases which form water, admit of an accurate determination by volume, while it is more difficult to determine them with precision by weight. If in the experiment of the formation of water, they were perfectly dry, or if the just correction were made for the quantity of water they hold dissolved, it would be of no importance whether the proportions were determined by weight or volume. But as the hydrogen combines with twice its volume of oxygen, and as in a given volume they hold dissolved the same proportion of hygrometric water, it is evident that in combining they do not carry into the combination quantities of water which are in the same proportions as those of the real ponderable matter of the oxygen and hydrogen. The relation too between the volumes of these gases will remain the same at all temperatures, and in all states of humidity, since they suffer the same degrees of expansion from a given elevation of temperature, and the same augmentation in their solvent power with regard to water. But the relation between their weights will, under these circumstances, be unequal, and this even to a considerable extent. Thus, in the experiment of Fourcroy, Vauquelin and Seguin above referred to, the proportions by weight are 85.662 of oxygen to 14.338 of hydrogen. But if the due

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[*] Journal de Physique, t. lx, p. 148.

correction were made for the water which the gases held dissolved, according to the estimate of Saussure, that a cubic foot of air at the temperature of 60 holds 10 grains of water in solution, it would follow, admitting the specific gravities which they assign to the gases, and the proportions in which they combine by volume, that the proportion by weight, instead of that which they state, is 87.41 of oxygen to 12.59 of hydrogen, and the same observation probably applies to the other experiments.

Gay-Lussac and Humboldt endeavoured to determine the proportions in which oxygen and hydrogen gases combine by volume. They fixed it at 100 of oxygen to 199.89 of hydrogen. It may, therefore, be stated without any error at 100 to 200. From the experiments of Fourcroy, Vauquelin and Seguin, the proportion is 100 to 205 ; by Monge it was fixed at 100 to 196, and Mr Dalton states it at 100 to 197. The medium estimate by Gay-Lussac and Humboldt, it can scarcely be doubted, is just, and is conformable to the law which regulates the combinations of aërial substances,—that they combine in relative quantities, having simple ratios estimated by volume. Converting these into the proportions by weight, according to the more accurate determination of the specific gravities of these gases by Biot and Arrago, they give as the composition of water 11.7 of hydrogen and 88.3 of oxygen, the proportion of 1 of the former to 7.5 of the latter. On this, accordingly, the relative combining weights of these two elements have been fixed in that proportion. If Dr Prout's estimate, however, of the specific gravity of hydrogen be admitted, the composition of water will be 11.1 of hydrogen and 88.8 of oxygen, the proportion of 1 of the former to 8 of the latter.

There are some other modes in which water is decomposed presenting some peculiar results. Its elements are separated and obtained insulated by the agency of electricity. This experiment was first performed by Troostwyk

and Deiman, assisted by Mr Cuthbertson ; and consisted in transmitting repeated electric discharges from a coated jar through a column of water in a tube *. By some variations it was rendered more easy of execution by Dr Pearson. The results in both were similar, gas was formed at each discharge, and this when accumulated sufficiently disappeared when inflamed ; or if it were removed, and mixed with nitrous gas, oxygen gas was discovered, by the production of red vapours, to the amount nearly of one-third of the volume, and hydrogen remained. There can be no doubt, therefore, that in these experiments water was resolved into oxygen and hydrogen gases, and again formed by their combination ; and as Dr Pearson has remarked, the evidence they afford in proof of the composition of water is peculiar, as in preceding experiments, by which water was decomposed, other substances were necessarily introduced, while in these water is the only ponderable substance concerned. The agency of electricity in producing these effects, is probably to be ascribed to the momentary high temperature it produces at the point at which it issues from or enters into the wire ; when it issues it is accumulated from the comparatively imperfect conducting power of the water, and when it enters it is condensed by the superior conducting power of the metal †.

Water is likewise decomposed by voltaic electricity. If a gold or platina wire be inserted in the top of a glass tube passing within it an inch or two, the aperture being closed, and if another wire rise from the bottom, to a little distance from the former, on connecting the one wire with one extremity of a galvanic battery, and the other with the other extremity, the tube being filled with water, a stream of gas rises from each, the water in the tube is depressed, and when a sufficient quantity of aëriform fluid is collect-

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* Journal de Physique, tom. xxxv, p. 369.
† Philosophical Transactions, 1797, p. 142.

ed to admit of examination, it is found to be a mixture of oxygen and hydrogen gases in the proportion which form water, so that if an electric spark be transmitted through it, it inflames, and entirely disappears, or at least leaves only a very small residue of nitrogen when the water has not been previously completely freed from air by boiling. Fig. 65. represents an apparatus in which this experiment is performed.

This decomposition of water by galvanism was formerly supposed to present a difficulty, in the circumstance that the two gases are not evolved at each wire, but the one is given out at the one, the other at the other, oxygen being evolved at the wire in connection with the positive or zinc end of the battery, and hydrogen from that in connection with the negative side : by placing the wires in separate tubes, placed in the same vessel of water, as in the apparatus, Fig. 66., each gas, if a gold or platina wire be used, may be collected pure ; or if a wire of an oxidable metal be used, such as silver, it is oxidated at the positive side, while hydrogen is evolved at the other.   The question occurred, therefore, what becomes of the oxygen at the wire where the hydrogen is given out, and what becomes of the hydrogen where the oxygen is disengaged.

To account for this different hypotheses were proposed. Monge supposed that water might exist with an additional proportion of each of its ingredients ; that at the positive wire it becomes super-oxygenated, and at the other it remains with an excess of hydrogen.   And it was maintained, what appeared to favour this hypothesis, that at the positive wire there is a production of acid, and at the negative a production of alkali.   The acid was affirmed by Pacchioni, Brugnatelli and others to be the muriatic, the alkali was stated to be potash or soda.   The fallacy, however, of these observations has been sufficiently established. A little nitric acid is liable to be produced at the positive wire when water is employed holding atmospheric air in

solution, from the oxygen of the water, as Cruickshank re-
marked, combining with the nitrogen of the air; and am-
monia may be formed at the negative side, from the hy-
drogen in its nascent state combining with another por-
tion of nitrogen. Or if the water contain the smallest por-
tion of saline matter, this, from the powerful action of gal-
vanism, will be decomposed, and its acid collected at the
positive wire, its alkali at the negative, as Davy pointed
out. But if care be taken to obviate these sources of fal-
lacy, it was proved by the experiments of Pfaff [*], and of
the Galvanic Society of Paris [†], as well as by Berthollet,
Biot, Thenard [‡], and Davy [§], that there is no sensible pro-
duction of acid or alkali; the water remaining pure to the
end of the process, and being resolved into oxygen and
hydrogen alone.

The separate evolution of the elements of water in its gal-
vanic decomposition is not peculiar to it, but is analogous
to the other cases of decomposition by this force. The law
with regard to this, established as a general one by the re-
searches of Berzelius and Hisinger, and illustrated more
particularly with regard to water by Grotthus, has been
already stated, (vol. i, p. 604). It is simply, that certain
substances have such a relation to the different electrical
states, that when placed in the voltaic circuit, some are
collected around the positive, others around the negative
pole; inflammable substances, alkalis, earths and oxides
being collected around the latter, oxygen and acids around
the former. When water therefore is submitted to gal-
vanic action, it suffers decomposition, and in conformity
to this law its hydrogen passes to the negative side, and

* Philosophical Magazine, vol. xxix, p. 19.
† Ibid. vol. xxiv, p. 172.
‡ Journal de Physique, tom. lxiv, p. 8.
§ Philosophical Transactions for 1807.

becoming insulated assumes the aërial form, while its oxygen is collected around the positive wire, where it also becomes insulated, and if the metallic wire does not combine with it, assumes the gaseous state. The mode of decomposition and conveyance is not apparent, but the operation may consist, as has been already stated, in the electric states being communicated to the elements of the water, and the attractions exerted in consequence of this at each pole overcoming their mutual chemical attraction, whence will arise their separation, and their transfer to the respective poles; the element which becomes negative passing to the positive side, and that which becomes positive passing to the negative side.

A singular hypothesis was advanced by Ritter, which some have been disposed to embrace. It assumes that water is a simple substance, which passes into the forms of oxygen and hydrogen according to its electrical states. When acted on therefore by voltaic electricity, its transition into these gases is not owing to its decomposition, but to these states being communicated to it; receiving positive electricity at the positive wire, it becomes oxygen, and receiving negative electricity at the negative wire, it becomes hydrogen. And when these gases are presented to each other, the different electricities are annihilated, and water is produced. This is a possible hypothesis, but there is no particular evidence in its support, nor any thing peculiar with regard to the action of galvanism on water, more than with regard to other substances, to lead to such a view: and it might as well be maintained, that when a compound salt is resolved, in the galvanic circuit, into an acid and an alkali, which are collected around the respective wires, it passes into acid and alkali from the electrical states communicated to it, as to advance the above hypothesis with regard to water. The result stated by Ritter, in proof of his opinion,—that of oxygen and hydrogen being evolved at the positive and negative wires, placed in

separate portions of water, when these are connected by a
metallic arc *, through which the ponderable elements of
the water cannot be supposed to be conveyed, though e-
lectricity might be communicated, I have already stated,
(vol. i, p. 608), is a deceptive appearance, the connecting
wire becoming electrical by induction, and the oxygen
and hydrogen being given out at its extremities corre-
sponding to the oxygen and hydrogen disengaged at the
galvanic wires.   This hypothesis, therefore, has no evi-
dence in its support.

In the combination of oxygen and hydrogen, there are
the peculiarities of the combination taking place only in
one proportion, and of the compound having no acid nor
alkaline powers.   The properties, therefore, of these ele-
ments are mutually neutralized ; the principle accounting
for this result has been already explained.   The degree
of condensation attending the combination is very great,
the volume of the elements being reduced in water to
$\frac{1}{2000}$.   On this condensation and perfect neutralization,
probably depends the weak chemical action which the com-
pound exerts.

Although water does not exert very energetic affinities,
so as to combine intimately with bodies, and alter their
properties, still it is an important chemical agent, from
combining with many substances, and, without modifying
much the order of their attractions, communicating that
fluidity which is requisite to chemical action.   Hence it
is a common medium, in which substances are brought to
act on each other ; and so little does it modify their at-
tractions, that its action is seldom considered in the theory
of the operations in which it is thus concerned.   There
are many cases, however, in which it is not so inert.

Water is tasteless, colourless and inodorous.   It passes

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* Nicholson's Journal, 4to, vol. iv, p. 512.

into the solid form at 32° of Fahrenheit, and suffers regular crystallization. This is seen in the slow congelation of water, prisms shooting from the sides of the vessel, and from each other, at a certain angle, that of 60° or 120°, and also in the radiated appearance of a flake of snow. The figure of the crystals of ice, according to Hassenfratz *, is that of a hexaedral prism ; in hail, it is that of an octaedron. By the continuance of the crystallization, the vacuities between the crystals are filled up, and a solid, brittle and transparent mass is formed, the state in which ice usually occurs. When heat is communicated to ice or snow at 32°, fusion takes place, accompanied with an absorption of caloric, from an enlargement of capacity. There is, at the same time, a diminution of volume, water at 32° being more dense than ice at the same temperature. This diminution of volume continues to proceed, (as has been already stated under the history of expansion), as the temperature is raised several degrees above 32° ; the greatest density of water is about 40° of Fahrenheit ; and as it recedes from that temperature, either to a higher or lower, it expands in an increasing ratio. In the act of freezing it exerts a strong expansive power : a quantity of air which the water held dissolved is expelled, and hence the ice is porous : but the expansive force, and probably also the enlargement of volume as it approaches the freezing point, are principally owing to the new arrangement into which the particles pass.

Even at a temperature below 32°, ice passes into vapour when exposed to the atmosphere, undoubtedly from the affinity exerted towards it by the gases composing atmospheric air. Water likewise evaporates slowly at a low temperature ; the evaporation becomes more copious as the temperature is raised ; it boils under the mean atmospheric pressure at 212° ; *in vacuo* at about 90° of Fah-

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* Journal de Physique, tom. xxxiii, p. 57.

renheit; and in passing at any temperature into vapour, it absorbs a quantity of caloric, which becomes latent; this latent caloric, according to Mr Watt's observation, being less as the temperature of the water from which it is produced is greater; in other words, being less when produced under a greater pressure, than under a less pressure [*].

When the vapour of water is fully formed, it is transparent and invisible; when condensing, a degree of opacity arises from the approximation of its particles. It occupies at 212°, according to Mr Watt, nearly 1800 times the space which water does; its specific gravity is to that of atmospheric air at the same temperature, according to Saussure, Tralés and Dalton, as 7 to 10 nearly; 100 cubic inches weigh 21 grains. The elastic force it exerts is increased by elevation of temperature, and, according to Mr Dalton's experiments, nearly in geometrical progression. He has given a table of this force for a considerable range of temperature, which has been already inserted, as well as the table, with results somewhat different, which has been given by Betancourt, (vol. i, p. 277, 278)

By a sufficient reduction of temperature, or by subjecting it to sufficient pressure, steam returns to the state of water, and gives out its latent caloric.

Water is slightly compressible. This was proved by Canton, by including it in a glass flask, with a narrow neck, and removing the pressure of the atmosphere by the air-pump: it rose a little; when the pressure was augmented by the condenser, it fell.

Water is capable of absorbing all the gases, but in very different quantities, according to the affinity which it exerts towards them. Of some of the acid gases it absorbs many times its own bulk, while of others the quantity absorbed is so inconsiderable, as to require an apparatus of

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[*] Philosophical Transactions, vol. lxxiv, p. 335.

some delicacy to measure it. This has been made the subject of experiment by Dr Henry. Of the three simple gases, oxygen, nitrogen and hydrogen, the two latter are absorbed in nearly equal quantity, 1.5 by 100 of water previously freed from air by boiling; that of oxygen amounts to 3.5. According to Gay-Lussac and Humboldt, the difference is even greater. In exposing 100 measures of each gas to a certain quantity of river water, the oxygen diminished 40 parts, while the nitrogen lost only 5, and the hydrogen 3 : and the diminution of oxygen was even greater than this; for the residual 60 measures, instead of being pure oxygen, contained 37 of nitrogen gas which had been expelled from the water by the oxygen, so that the real absorption of the oxygen gas had been 77. The nitrogen expels in like manner, when it is absorbed by water, a portion of oxygen; its real absorption, therefore, is between two and three hundredths. Hydrogen they found to be scarcely sensibly absorbed [*]. Saussure has more lately stated results [†] which are also different. With regard to these three gases, in particular, he finds that 100 volumes of water absorb 6.5 of oxygen gas, 4.6 of hydrogen, and 4.1 of nitrogen; and of atmospheric air about 5 volumes, when the mass of air is great in comparison with that of the water. A table of his results is given beneath. According to Mr Dalton, Saussure's conclusions are wrong with regard to the less absorbable gases from the fallacy attending the method of employing much air relative to a small quantity of water. The degree of absorption he considers as not much more than one-half of what Saussure states. The proportion of oxygen gas he estimates at 3.7 or 4 per cent. of the water, that of nitrogen gas at 2.5, and that of hydrogen gas at 2 [‡].

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[*] Journal de Physique, tom. lx, p. 165.
[†] Annals of Philosophy, vol. vi, p. 338.
[‡] Ibid. vol. vii, p. 218.

The following table shews the quantities of gases absorbed by water at the temperature of 60°, and under a mean atmospheric pressure. The first nine are on the authority of Henry. With regard to all of them, there are some differences in the experiments of different chemists, as is noticed under their history.

Gases.	Cubic inches absorbed by 100 cubic inches of water.
Oxygen gas,	3.55
Nitrogen gas,	1.47
Hydrogen gas,	1.53
Carburetted hydrogen gas,	1.40
Phosphuretted hydrogen gas,	2.14
Sulphuretted hydrogen gas,	108.
Carbonic oxide gas,	2.01
Carbonic acid gas,	108.
Nitric oxide gas,	5.
Nitrous oxide gas,	77.6
Olefiant gas,	12.5
Sulphurous acid gas,	3300
Muriatic acid gas,	42100
Oxymuriatic acid gas,	200
Ammonia,	41000

Saussure has given a table of the results of his experiments on the absorption of the gases by water, to which he has added a column showing their corresponding absorption by alkohol.

Gases.	100 volumes of water.	100 volumes of alkohol, sp. gr. 0.84.
Sulphurous acid gas,	4378	11577
Sulphuretted hydrogen,	253	606
Carbonic acid,	106	186
Nitrous oxide,	76	153
Olefiant gas,	15.3	127
Oxygen gas,	6.5	16.25
Carbonic oxide,	6.2	14.5
Oxy-carburetted hydrogen,	5.1	7
Hydrogen,	4.6	5.1
Nitrogen,	4.1	4.2

The quantities of gases absorbed by water are greater as the temperature is low, until the water freezes, when it parts with those to which its attraction is weak, while those to which it is stronger are retained. The absorption is also aided by pressure. Dr Henry, from experiment, stated, with regard to those gases which are absorbed in small quantity, the important general law, " That under equal circumstances of temperature, water takes up, in all cases, the same volume of condensed gas, as of gas under ordinary pressure." Hence, as the spaces occupied by every gas are inversely as the compressing force, it follows, " that water takes up, of gas condensed by one, two, or more additional atmospheres, a quantity which, ordinarily compressed, would be equal to twice, thrice, &c. the volume absorbed under the common pressure of the atmosphere." By increasing pressure, therefore, a very large quantity of any gas may be made to be absorbed by water; and by various mechanical contrivances, water may be impregnated strongly with the different aëriform fluids. Paul of Geneva has thus combined large quantities even of those gases which are very sparingly soluble in water. According to his statement, water is made to absorb half its volume of oxygen gas, one-third its volume of hydrogen, and two-thirds of carburetted hydrogen. It is somewhat singular, that the water impregnated with these gases acquires no new properties. It differs little from common water in taste, produces no effervescence on being uncorked, nor affords, by the test of re-agents, appearances which would indicate clearly the presence of the gas with which it had been impregnated. The small portion of gas which could be extracted was found to be that with which the water had been impregnated, tolerably pure *.

Mr Dalton has considered the absorption of gases, thus

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* Report to the National Institute on Paul's Artificial Mineral Waters, p. 20.

produced by pressure, as a mechanical effect; the gas by
the pressure being forced into the interstices of the fluid,
and existing in it, with its elasticity unimpaired, precisely
as without, so that when the pressure is removed it escapes
in its elastic form ; and he has considered the law disco-
vered by Dr Henry, as regulating the absorption, as a
proof of this, the quantity absorbed being proportional to
the pressure applied, and the pressure, therefore, being in-
ferred to be the sole cause of the absorption.   A different
view, however, may be given of this subject.   In the ab-
sorption of gases by water, two powers operate, or may be
conceived to operate, independent of pressure,—the affi-
nity between the gas and water tending to combine them,
and the elasticity of the gas counteracting this, and placing
limits to the combination.   Whatever favours the exer-
tion of the elasticity will lessen the quantity absorbed ;
whatever represses it, will promote the absorption.   These
effects are produced by variations of mechanical pressure ;
the diminution of pressure favouring the exertion of elas-
ticity proportional to the degree in which it is applied.
But from this no just argument can be drawn against the
conclusion, that a chemical affinity exists, and is the pri-
mary cause of the combination, and the law stated by Dr
Henry is just as conformable to the one theory as to the
other.

A proof that this view is just, is, that the effect of pres-
sure is the same in increasing the absorption of those gases,
between which and water the existence of a chemical affi-
nity is so evident, that it cannot be denied, as, for exam-
ple, muriatic acid gas.   There is no difference but in the
quantity absorbed being larger, from the exertion of a more
powerful affinity, in the one case, than in the other. This,
it is obvious, introduces no essential difference into the na-
ture of the operation; and it would be easy, by making
experiments on all the gases, to form a series of quantities
absorbed, from that which is greatest to the least ; so that

it would be impossible to point out the line of distinction between those where the absorption might be conceived to be mechanical, and those where the exertion of affinity must be allowed to operate.

Mr Dalton has said, in answer to this *, that " nothing is more easy than to point out the exact line of distinction : wherever water is found to diminish or destroy the elasticity of any gas, it is a chemical agent; wherever it does neither of these, it is a mechanical agent." But where is the proof that in any case the elasticity of a gas absorbed by water remains ? Carbonic acid, which is considered as mechanically absorbed by water, is, so far as we can discover, in the same state as muriatic acid, which is admitted to be chemically combined. Remove pressure from the liquid, and portions of both will escape. The only difference is, that as the affinity of water to muriatic acid is stronger than to carbonic acid, more of the former is absorbed under a given pressure ; and for the same reason, when the pressure is removed, more of it will be retained ; otherwise the two cases are alike. It is even proved, that the same law regulates the absorption of those gases by water in which the operation of chemical affinity is undoubted, as of those in which it is supposed to be merely mechanical. Saussure, for example, found that sulphurous acid gas, one of those which suffers the greatest absorption, is absorbed by water, in the same volume, whatever may be its density from pressure,—the very law established by Henry, and the basis of Mr Dalton's reasoning †.

Another proof that the absorption is not owing merely to pressure, is, that the quantities of the gases, absorbed under the same pressure, are different. Thus water exposed to atmospheric air absorbs a larger portion of oxygen than of nitrogen, in the proportion of 3.5 to 1.5; yet

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* System of Chemical Philosophy, p. 206.
† Annals of Philosophy, vol. vi, p. 344.

the pressure of the column of oxygen gas in the atmosphere, producing, according to Mr Dalton's view, its absorption, is equal only to that of 7.8 inches of mercury, while that of nitrogen is equal to 21.2.   The quantity of nitrogen absorbed, therefore, by water, exposed to the atmosphere, instead of being inferior to the quantity of oxygen, ought, according to this view, to be nearly three times greater ; and no cause can be assigned for the difference but the affinity which is exerted to these gases by water. A similar fact is, that under a given pressure, a much larger quantity of carbonic acid gas than of oxygen or nitrogen gas is absorbed by water,—equally proving the influence of elective affinity in determining the absorption.

If the absorption in these cases be a mechanical effect, it ought to be the same in other fluids ; while, if dependent on affinity, it may be expected to be different.   Mr Dalton accordingly stated, that most liquids free from viscidity, as acids, alkohol, &c. appear to absorb the same quantity of gases as pure water.   Of this, however, there was reason to doubt.   Davy had found, that nitrous oxide gas is absorbed in larger quantities by alkohol or ether, and even, notwithstanding their viscidity, by essential and expressed oils, than by water.   And more lately, Th. Saussure has shewn, both that different liquids, alkohol, ether, oils, and saline solutions, absorb very different quantities of the same gas, and that the same liquid, oil, naphtha, or a saline solution, absorbs very different quantities of the different gases. Thus 100 volumes of naphtha absorb 261 of olefiant gas, 254 of nitrous oxide, 169 of carbonic acid, and 20 of carbonic oxide.   100 volumes of essential oil of lavender absorb 275 of nitrous oxide, 209 of olefiant gas, 191 of carbonic acid, and 15.6 of carbonic oxide.   100 volumes of olive oil absorb 151 of carbonic acid, 150 of nitrous oxide, 122 of olefiant gas, and 14.2 of carbonic oxide. And 100 volumes of a saturated solution of muriate of potash absorb 61 of carbonic oxide, 21 of nitrous oxide, 10

of olefiant gas, and 5.2 of carbonic oxide. Carbonic acid gas is absorbed in larger quantity by alkohol, ether, and oils, both expressed and volatile, than by water, and in larger quantity by water than by saline solutions *.

From the experimental researches of Mr Dalton and Dr Henry on the absorption of gases by water, several important facts, independent of all theory, have been established. Thus, if water be agitated with a mixture of two or more gases, portions of both will be absorbed, the same as if they were presented to it separately in their proper density; the quantity therefore being greatest of that which separately is most largely absorbed by water. Or, if water has been previously impregnated with one gas, on agitating it with another, a portion of the latter will be absorbed, and a portion of the former be displaced. This fact had been long known. It had been remarked by Dr Brownrigg, in the example of mineral waters impregnated with carbonic acid, from which the gas escapes when they are exposed to the air; while, when excluded from the air, although liberty be given for the gas rising into an empty bladder, it does not separate. Hence, as water usually contains a portion of atmospheric air, on agitating any pure gas with it, a quantity of this is absorbed, and a portion of the air the water held dissolved is separated, and added to the residual gas. This has been sometimes a source of error in chemical experiments; and even in transmitting a gas through water, a small degree of admixture must, from the same cause, take place. This effect must, on the chemical theory, be ascribed to the affinity of the one gas to the water weakening the affinity of the water to the other, and in part perhaps to the affinity exerted between the gases themselves.

From these facts, the relation of water to atmospheric air may be understood. If agitated with it, a portion is

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* Annals of Philosophy, vol. vi, p. 341-342.

absorbed; but the two chief constituent gases of the at-
mosphere, the oxygen and nitrogen, are not equally af-
fected, the former being absorbed in preference to the lat-
ter.   This was long ago observed by Scheele; he found,
that when atmospheric air was confined in a vessel with
water that had been boiled to free it from air, it diminish-
ed in volume, and the residual air was at length incapable
of supporting combustion *.   Priestley observed, too, that
water agitated with atmospheric air absorbed the oxygen
in preference to the nitrogen.   Berger has shewn, that by
repeatedly transmitting atmospheric air through a column
of water, it suffers this decomposition, and that thus the
whole of its oxygen nearly is abstracted †.   Sometimes,
however, the presence of one gas in water causes a lar-
ger portion of another to be absorbed.   Thus, the pre-
sence of oxygen favours the absorption of nitric oxide gas,
and even of hydrogen, according to the observation of De
Marti ‡.   This has been confirmed by Gay-Lussac and
Humboldt, who, in exposing a mixture of oxygen and hy-
drogen gases to water, found, that with the oxygen a con-
siderable quantity of hydrogen was absorbed, though the
hydrogen by itself scarcely suffered any loss.   The mixed
hydrogen and oxygen they found to be expelled again from
the water by heat ; they had not therefore combined inti-
mately, but still the effect must be ascribed to the affinity
of the one gas to the other.

Any aëriform fluid absorbed by water must, it is obvi-
ous from the preceding facts, be most effectually retained
in combination by the pressure of gas of its own kind.

De Marti found a result with regard to the absorption
of gases by water rather singular.   If water be repeatedly
agitated with an air, suppose oxygen, in a phial, it will be

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* Experiments on Air and Fire, p. 164.
† Journal de Physique, tom. lvii, p. 1.
‡ Nicholson's Journal, vol. xviii, p. 125.

saturated with it, and no farther absorption takes place. If the phial be accurately closed with a glass stopper, and put aside for a few days, on opening it under water, a portion will enter, shewing that part of the gas had been absorbed. If this be repeated from time to time, a fresh quantity of gas will be condensed, and the effect will be more perceptible the longer the air has been exposed to the water *. If the fact be established, it appears to prove that the combination is at first not perfect, but that it gradually becomes more intimate. This effect is rather greater with hydrogen gas, but it does not take place with nitrogen gas.

All water which has been exposed to atmospheric air, as spring and river water, contains a portion of air, from which it derives a sparkling quality and agreeable taste. Priestley observed, that this air has a larger proportion of oxygen than atmospheric air,—a result to be expected, since from air exposed to the action of water, a larger portion of oxygen than of nitrogen is absorbed. The air extracted from water by boiling being examined by Gay-Lussac and Humboldt, that from river water contained in 100 parts 31.9 of oxygen, from rain water 31, and from water which had been distilled, and exposed to the air, 32.8. Well water yields an air more variable, probably from the action of the saline matter it contains †. The air extracted from water appears too to contain a portion of carbonic acid. According to Henry, 100 cubic inches of spring water gave, by long boiling, 4.76 of gas, of which 3.38 were carbonic acid, and 1.38 atmospheric air ‡. This, however, is a larger portion of carbonic acid than appears to be usually contained in water. According to Dalton, the air expelled from spring water, after losing 5 or 6 *per*

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* Nicholson's Journal, vol. xviii, p. 125.
† Journal de Physique, t. lx, p. 160.
‡ Philosophical Transactions for 1803, p. 39.

cent. of carbonic acid, consists of 38 *per cent.* of oxygen, and 62 of nitrogen. Humboldt and Provençal state the quantity of air obtained from river water at about a thirty-sixth of the volume of the water, or 100 parts contain a-bout 2.8 by volume. This air, in repeated experiments for a number of months, they found to be the same in quality; the proportion of oxygen not varying more than from 0.309 to 0.314, and this is conformable to the experiments of Gay-Lussac with regard to the purity of the air contained in distilled water, in ice, in rain water, and in melted snow. It is only, however, from water that has been exposed to the atmosphere, that air of this standard is obtained. If the water is exposed to air in a close vessel, it neither absorbs the same quantity, nor does it take in the air of the same proportions. The proportion of carbonic acid that may be extracted from river water amounts, they found, to from 0.06 to 0.11 of the volume of the air yielded by the water; they ascribe its origin principally to the decomposition of a little vegetable extractive matter contained in river water : in spring water it may arise part-ly from the decomposition of carbonate of lime *. Gay-Lussac and Humboldt had found, that the presence of saline matter in water has an effect on its power of absorbing air. A quantity of air is disengaged during the solution of a salt in water, and a portion equivalent to this does not appear to be again absorbed : the air too, which is retained by the water, contains a larger proportion of oxygen than the air dissolved by pure water. According to Saussure and Dalton †, saline solutions absorb less of the different gases than pure water does : a solution of sea salt absorbs about a third less of gas.

The air held dissolved by water is expelled with great difficulty. If pressure be removed by the air-pump, part

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* Mémoires d'Arcueil, tom. ii, p. 369.
† Annals of Philosophy, vol. vi, p. 7.

of it is disengaged ; by strong boiling, a considerable por-
tion is expelled, and likewise by freezing : but a quantity is
still retained, which is not expelled by any of these means.
This is apparent in the experiment on the decomposition
of water by electricity, already referred to, (p. 123.) Dr
Pearson, although he endeavoured to free the water from
air by boiling, and by the air-pump, found that a portion
still remained, which was disengaged by the electric dis-
charge, and mingled with the gases from the decomposi-
tion of the water. It appears too, from the experiments
of Priestley, air being extricated in small quantities, but
apparently without limit, from water by repeated boiling,
though the water in the intervals of boiling, cooling, and
discharging the air, was confined over mercury so as not
to come into contact with the atmosphere : the same con-
tinued, but inconsiderable production of air, he observed,
by abstracting pressure from water confined over mercury
in a barometer tube, and also in the experiments already
related (p.26.) in the extrication of air from water by freez-
ing. According to Priestley's observation, the first portion
expelled is purer than that of the atmosphere ; the next
less pure, and at last it is, as he terms it, wholly phlogistica-
ted *, and this appears to be confirmed by the fact, that
when water has been freed as much as possible from air by
boiling, or by the air-pump, it is nitrogen which is dis-
engaged from it by freezing, or by the electric discharge.
Gay-Lussac and Humboldt, however, have affirmed, that
the air disengaged in successive portions from water by
heating and boiling it, contains more oxygen in the latter
portions than in the first, the first portion containing in
100 parts 23.7 of oxygen, the second 27.4, the third 30.2,
and the fourth 32.5. Melted ice, they found, did not give

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* Additional Experiments on the Generation of Air from
Water, p. 22.

more than half the quantity of air which common water
gives; and it contained a larger portion of oxygen, the
proportion in the first quantity that had been expelled con-
taining 27.5 of oxygen, in the second quantity 33.5. The
oxygen, therefore, appeared to be retained with more force
than the nitrogen, and the nitrogen must predominate in
the air disengaged in freezing [*].

The presence of oxygen loosely combined in water,
which has been exposed to atmospheric air, Scheele sup-
posed to be discovered by dissolving in it a small quantity
of green sulphate of iron. If the water be entirely free of
oxygen, and the vessel stopt, the solution is transparent;
but if otherwise, it becomes slightly turbid, from the oxide
of iron attracting the oxygen, and a small portion of it in
this more highly oxidated state, forming a yellow precipi-
tate, is thrown down. The partial decomposition of the
sulphate may be owing in part to the affinity of the water
to the acid, abstracting a portion of it; and accordingly,
it has been stated by Darso [†], that the precipitate takes
place equally in using common distilled water, and distil-
led water from which the air had been completely expel-
led. Still the production of the yellow oxide, from the ad-
dition of the green sulphate of iron, denotes an addition of
oxygen. And Mr Dalton has lately pointed out a similar
experiment, as the easiest mode of discovering the loosely
combined oxygen in water. The water submitted to trial
is mixed with a sixth part of lime water, solution of green
sulphate of iron is added in small quantity, and in half an
hour a precipitate of pure yellow oxide of iron subsides.
When the loose oxygen is exhausted, the addition of the
sulphate gives only a precipitate of a green colour. The
same effect is produced on adding a little of a solution of
potash to water, with a portion of the solution of the green

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[*] Journal de Physique, tom. lx, p. 160.
[†] Nicholson's Journal, vol. xvii, p. 275.

sulphate. The quantity of oxygen may be estimated by allowing $\frac{1}{9}$ of the weight of the yellow oxide as the quantity it has thus received from the water. By the same method, water may be freed from this free oxygen *.

From the difference in the affinities which water has to oxygen and to nitrogen gases, and from the fact that one gas exposed to water displaces more or less of another, is explained a circumstance, which has been the source of some fallacies, and which in experiments in pneumatic chemistry requires to be attended to. If a quantity of oxygen gas be kept in a jar which is inverted and placed in water, its purity is gradually diminished, a quantity of nitrogen gas is found to be mixed with it; and if it be kept long in this situation, the quantity of nitrogen will be considerable. This is owing to the water exposed to the atmosphere imbibing both oxygen and nitrogen; and the nitrogen being retained by a weak affinity, the pure oxygen in the jar, by the superior attraction which it has to water, detaches it, and thus receives a portion of it. Hydrogen gas is affected in a similar manner, nitrogen mixing with it when it is kept over water which is in contact with the atmosphere; and all gases, in such a situation, become impure.

Water which has descended slowly through the atmosphere may be expected to be saturated with oxygen, and accordingly Hassenfratz stated, that dew, rain-water, and snow, contain more oxygen loosely combined than water does in its usual state. Air from rain-water, he affirmed, suffers a diminution of volume by exposure to phosphorus, equal to 35 in 100; while air from the water of the Seine gave a diminution of only 20. To prove the presence of oxygen in snow, he gave the following experiment: 1000 grammes of snow were put into one jar, and 1000 grammes of distilled water in another; into each was poured an

* Annals of Philosophy, vol. vii, p. 219.

equal quantity of infusion of turnsol ; both were placed in
a warm temperature ; and after the snow melted, the dye
of the snow-water was found to be deeper than that of the
other. The experiment was repeated with sulphate of iron.
To 1000 grammes of snow, and 1000 of distilled water in
separate jars, were added pure sulphate of iron, 6.5 gram-
mes to each. In the first the precipitate of oxide of iron
amounted to 0.150 grammes, and in the other only to
0.010 *. To this larger proportion of oxygen, Hassen-
fratz ascribed the supposed fertilizing quality of snow. His
experiment, however, does not prove that snow contains
more oxygen than water which has been exposed to the
air ; as the comparison was instituted, not with water in
this state, but with distilled water. Carradori endeavour-
ed to shew, that snow-water is even destitute of that loose-
ly combined oxygen which is present in common water,
fishes put into it dying sooner than in common water,
when the renewal of air is equally prevented in both cases
by a layer of oil on the surface of the water ; but when the
snow-water has been exposed for some time to the air, the
fish are capable of living in it much longer. He adds,
that snow-water exposed to the action of light does not
give out oxygen †. Bergman too, remarked, that although
snow-water affords some traces of nitrous acid, it is when
newly melted totally void of air ‡. And from an experi-
ment by Saussure, on the air from the interstices of snow,
it appears to be less pure than atmospheric air §. Gay-
Lussac and Humboldt, on the other hand, affirm, that on
melting snow newly fallen, and heating the water, it afford-
ed nearly double the quantity of air that melted ice did,
and nearly as much as river water does. This air, col-

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* Philosophical Magazine, vol. iii, p. 237—38.
† Journal de Physique, t. xlviii, p. 226.
‡ Essays, vol. i, p. 114.
§ Voyages, t. vii, p. 472.

lecting the whole quantity of it, contained a quantity of oxygen equal to 28.7 in 100 parts. The quantity of air, according to these chemists, disengaged from snow-water by boiling, amounts to about $\frac{1}{25}$th the volume of the water, and the quantity from river water is nearly the same. The discordance of these results probably arises from the varying porosity of snow in different states.

Ritter affirmed, that oxygen is disengaged from water by freezing. He had remarked, that when it is frozen under the influence of galvanism, the portion at the *minus* side of the pile freezes sooner than that at the *plus* side, which he ascribed to the water in the former situation having an excess of hydrogen, in the latter an excess of oxygen. This led him to examine the air disengaged in freezing, and as it is not easily collected, so as to be submitted in any quantity to examination, he endeavoured to discover the nature of it by re-agents. He mixed muriatic acid with water, and suspended a stripe of gold leaf in it. On causing the liquid to freeze, a minute portion of the gold appeared to be dissolved, whence it might be inferred, that oxygen had been disengaged from the water in freezing, which converted the muriatic into oxymuriatic acid, so as to enable it to act as a solvent on the metal. Green oxide of iron was diffused in water; and on the water freezing, the oxide acquired a yellow colour, as it does when it receives oxygen. And having diffused in portions of water white prussiate of iron, (a substance which, by the blue colour it assumes, when it receives oxygen, is a very delicate test of that principle,) excluding the action of the air by a thin layer of oil on the surface of the liquid, on exposing them to unequal degrees of cold, as often as any portion froze, the white precipitate became blue. By some subsequent experiments he endeavoured to shew, by the blackening of muriate of silver, exposed to melting ice, that the ice gives out hydrogen in passing to the state of water. These experiments have not been confirmed, and if they

were, it would remain doubtful, whether the effects were not owing to the separation of the oxygen not essential to the composition of water, but held by it in a state of solution, the last portions of it being retained with much force, and being disengaged by the freezing.

Water is contained in all the gases, derived either from the materials from which they have been extricated, or from the water through which they are transmitted. It exists in general in vapour, in a state of loose combination, not modifying their properties : it may be condensed by cold, a film of ice being formed on the containing vessel, when the temperature is reduced to 0°; and it may be abstracted by exposure to such bodies as have a strong attraction to water, as potash, lime, or muriate of lime. This is named Hygrometric Water, or Vapour. Its quantity is in a great measure dependent on the temperature augmenting, however, in atmospheric air, and probably in all the gases, in a higher ratio as the heat is raised, than the arithmetical progression of temperature, as has been already stated (page 58).

Besides this hygrometric aqueous vapour in elastic fluids, it has also been inferred, that water exists in some gases in much larger quantity, in a more intimate state of chemical combination. Many of the results, however, by which this was supposed to be established, have been shewn to be doubtful or incorrect. Thus, Priestley observed, that when the electric spark is taken in carbonic acid gas, it suffers enlargement of volume, and is no longer entirely absorbed by water. Monge observed the same phenomena, and also that there is an evolution of an inflammable gas,—effects which were ascribed to the decomposition of water contained in it, and regarded therefore as proofs of the existence of combined water in carbonic acid gas. It is the acid itself, however, that is decomposed. T. Saussure found, that the gas evolved is not hydrogen, but carbonic oxide, the copper wire employed to transmit

the spark, attracting part of the oxygen of the carbonic acid, and giving rise to the formation of this product Dr Henry found, that the augmentation of volume takes place when the electric spark is communicated by platina wires, which are not oxidable; and this expansion was accompanied with the evolution of oxygen and of an inflammable gas *. But this equally might be carbonic oxide, from a partial decomposition of the acid; and he accordingly afterwards found, that the acid is decomposed, and resolved into oxygen and carbonic oxide †. Similar results had been observed with regard to another elastic fluid, the heavy inflammable air, or carburetted hydrogen. Dr Austin found ‡, that by electricity it is expanded to twice its original volume, and there appeared to be an addition of inflammable matter, as the expanded gas required more oxygen for its saturation than the original gas; whence it might be inferred that water had been decomposed, its oxygen being retained by the wire conveying the spark, and its hydrogen being set free. The principal result, however, the enlargement of volume, might arise from the decomposition of the gas; and it appears from Dr Henry's experiments, that this is the case : there is an e-volution of a portion of hydrogen, while the charcoal with which this had been combined is precipitated §. In this case there is no addition of inflammable matter, and the slight addition of this kind in the experiments of Austin might be owing to the decomposition of the small portion of hygrometric water, diffused through the gas.

There is another class of facts which have been suppos-ed to prove that combined water exists in carbonic acid gas. Withering observed, that the native carbonate of barytes cannot be decomposed by heat while the artificial carbonate is decomposed easily, which he attributed to

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* Philosophical Transactions 1800, p. 203.
† Ibid. 1809.   ‡ Ibid. 1790, p. 51.   § Ibid. 1809.

water being contained in the artificial carbonate, and promoting by its affinity to the carbonic acid its separation. Priestley apparently confirmed this opinion, by finding that when the vapour of water is passed over the native carbonate at a red heat, the carbonic acid is expelled. Some varieties of native carbonate of lime exhibit the same phenomenon to a certain extent; and the expulsion of the acid in the common process of calcining limestone, Berthollet supposes to be favoured by the watery vapour from the burning fuel. Gay-Lussac and Thenard have likewise found, that the admission of water favours its expulsion from lime by heat * : and they have farther shewn, that the expulsion of carbonic acid from subcarbonate of potash or of soda takes place when watery vapour is applied, while it does not, according to Darcet's experiments, when they are heated alone in close vessels. But in all these cases the water acts not from the affinity it exerts to the carbonic acid, but from its attraction to the barytes or lime; and accordingly, carbonic acid is expelled by heat without the presence of water from other bases, to which it has a less strong attraction, and in relation to which, water exerts no peculiar power. Carbonic acid also, in some of its combinations, cannot be expelled by the affinity of another acid to the base with which it is combined, unless water be supplied. Thus, it is not disengaged from the native compound of it with barytes by muriatic acid, unless the acid be diluted. But still the agency of the water in this case depends on its relation to the barytes, and not to the carbonic acid.

There is one gas in which the proofs appeared more conclusive of the existence of a considerable portion of water in a state of intimate combination,—muriatic acid gas. When submitted to the action of electricity, hydrogen is evolved from it, and this even when it has been previously exposed to the action of muriate of lime, a sub-

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* Recherches Physico-Chemiques, tom. ii, p. 184.

stance which exerts the strongest attraction to water. When metals which have a strong attraction to oxygen, as iron or zinc, are submitted to its action, there is a similar evolution of hydrogen, and the metal suffers the same change as it does from the action of the liquid acid in which the decomposition of water is undoubted. Gay-Lussac and Thenard found also, that water is produced when the gas is transmitted over metallic oxides, as oxide of lead; and from the quantity of it they inferred, that combined water exists in the gas to the amount even of one-fourth of its weight. A different hypothesis, however, has been proposed with regard to the constitution of this acid, in which the existence of combined water in the gas is denied, and it is considered as being formed in those cases in which it is obtained, from the combination of hydrogen, existing as a constituent ingredient of the acid, with oxygen derived from the substance acting upon it: And even independent of this, it is probable, that the elements of water, rather than water itself, exist in muriatic acid. This will be considered under the theory of acidity and the history of muriatic acid.

Gay-Lussac and Thenard, with a view to elucidate this subject, availed themselves of an agent which they had discovered, which is powerful in detecting aqueous vapour,— the Fluo-boric acid. It exists in the gaseous form; and so strong is its attraction to water, that when mingled with atmospheric air in its usual state, it forms dense vapours, by combining with the hygrometric vapour of the air; and by the same appearance it discovers the presence of hygrometric water in any other elastic fluid. They found, that on adding this gas to atmospheric air, saturated with humidity, very dense vapours were formed; but when these were condensed, a fresh portion produced no appearance of this kind, a proof that the first quantity had abstracted the whole water: with air at a medium dryness, a cloud was formed; but with air which had been

exposed for five hours to quicklime, there was no sensible
production of vapour, though if to this dry air a fiftieth of
the volume of humid air were added, it immediately ap-
peared. With the other gases similar results were ob-
tained. These chemists likewise exposed the different
gases to a degree of cold lower than that of freezing wa-
ter, by which vapour diffused in them is condensed. As
the general result, they found, that all the gases which
are not very soluble in water, and even some which are
more soluble, such as carbonic acid gas, nitrous oxide gas,
oxymuriatic acid gas, and sulphurous acid gas, may con-
tain hygrometric water, but there is no reason to suppose
that they contain combined water : they can be formed
from ingredients free from water ; and some of them,
as nitrous oxide, and carbonic acid gas, when decompos-
ed by potassium, give no hydrogen, which they would do,
did they contain combined water. Muriatic acid gas ap-
peared to contain no hygrometric water ; for when ex-
pelled from water which held it in solution, and received
over quicksilver, the admission of the fluo-boric gas did
not give rise to the slightest cloud, nor when exposed to
great cold did it deposite any humidity ; and they add
the converse proof, that a drop of water, when intro-
duced to this gas, did not diminish, which it would have
done had the gas been capable of elevating it in hygro-
metric vapour. This absence of hygrometric vapour in this
gas appears to arise from the circumstance, that if com-
bined with the smallest portion of water it passes to the
fluid form. Fluo-boric gas itself, they infer, contains no hy-
grometric water, as a drop of water introduced into it suffer-
ed no diminution. Neither does it afford hydrogen when
acted on by potassium, and therefore it does not appear to
contain combined water. Ammonia yielding no trace of wa-
ter, or of oxygen when decomposed, the inference follows,
that it contains no combined water. From Dr Henry's
experiments it appears that it may contain a little hygro-

metric water, as when exposed without previous desicca-
tion to a cold of 0° of Fahrenheit, a thin film of ice is de-
posited on the sides of the vessel. This appearance is not
obtained from muriatic acid even at a cold of —26.

The general result on this question is, that the gases
usually contain a portion of hygrometric vapour, which
they receive from the presence of water in the processes
by which they are obtained. But this is not essential to
them ; it may in a great measure be abstracted by expo-
sure to intense cold, or by the action of substances having
a powerful attraction to water, such as potash, muriate of
lime, or sulphuric acid. The entire abstraction is diffi-
cult; for in proportion as the vapour is withdrawn, the re-
maining portion expands, and from its great rarity, the
affinity of the substance acting upon it cannot overcome
its elasticity. But the quantity thus remaining, when a
powerful hygrometric substance is employed, must be ex-
tremely inconsiderable, and altogether inappreciable.

Water is the general solvent of saline substances. It
combines with the acids and alkalis, condensing those of
them which are gaseous, and dissolving those which are
solid usually in large quantity. It dissolves the greater
number of the neutral salts ; it passes into combination
with them when they crystallize, and they retain the last
portions of it with the greatest force, so that it cannot be
entirely expelled by a red heat.

The general chemical agency of water appeared to be
merely this, of acting as a solvent,—overcoming cohesion,
in solids, diluting liquids, and absorbing gases ; without
entering into intimate combination in definite proportions,
or giving rise to any important modification of properties.
Some facts, however, more recently established, appeared
to prove, that its operation as a chemical agent is often
more important.

It has thus been inferred, that it is necessary to the con-
stitution of the more powerful acids in an insulated state.

It is obtained, as has been just stated, in a definite and large proportion from muriatic acid gas, and the acid cannot be disengaged from its combinations without water being supplied, and of course cannot be obtained free from it. Nitric and sulphuric acids cannot be formed without the presence of water; it is necessary, for example, to the formation of nitric acid, by the union of oxygen and nitric oxide gases; and, as Gay-Lussac and Thenard have remarked *, if it were possible to abstract the water of nitric acid, it would probably be resolved into these gases. The formation of sulphuric acid, by the union of sulphurous acid and oxygen gases, is equally determined by the presence of water, so that if water is excluded it does not take place. When these acids, too, are saturated with any base, a large quantity of water is obtained from them, and they are separated from their combinations only when water is supplied. Fluoric acid is equally incapable of being obtained, insulated without water. And it deserves to be remarked, that these four acids, to the separate existence of which water is necessary, are the most powerful of the whole class. Other acids, as the boracic and phosphoric, retain it with great force.

The attraction of the Alkalis to water is equally strong. Potash and soda, in the driest state to which they can be brought, contain a definite quantity of it, which cannot be expelled by heat. The alkaline earths have a similar relation to it. Barytes, even after fusion, retains nearly one-tenth of its weight of water. It is also absorbed by strontites, and by lime with great force, and is not easily separated. The powerful affinity of water to the alkalis and earths is also proved by the facts already stated, with regard to its influence in facilitating the disengagement of carbonic acid from the combinations they form with it. Many of the metallic oxides likewise appear to retain it in

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* Recherches, tom. ii, p. 181.   Mém. d'Arcueil, tom. ii, p. 356.

intimate combination. Compounds in which water thus exists in a definite proportion have been denominated Hydrates.

These facts had been considered as conclusive, in proving that water exists in intimate combination with these bodies, and as materially modifying their chemical properties and relations. According to a view which I have suggested, however, to be afterwards illustrated, it is more probable, that in all these cases the elements of water rather, that is, oxygen and hydrogen, in the proportion which forms water, are present in simultaneous combination with the other elements of the combination, and do not exist in the state of water itself; and we thus avoid the apparent anomaly in the action of water when there are ascribed to it, powers so much more energetic than those which it usually exerts.

Water exerts a solvent effect even on those earths to which it does not display any strong attraction. By some of them it is imbibed and retained with considerable force, others it retains for a long time in a state of suspension; and earthy compounds which it cannot dissolve, it wears away and reduces to extreme division, partly by attrition, and partly by its chemical powers. This effect gave rise to an opinion once entertained, that it is convertible into earth. Boyle observed, that water, when distilled even 200 times, deposited each time a quantity of earth, and was itself diminished in the experiment,—observations which were confirmed by succeeding chemists. A more attentive examination shewed, that the origin of the earth was from the glass vessels employed in the operation. A striking experiment in proof of this is given by Scheele, and which demonstrates the chemical action of water on glass, when it is aided by a high temperature. A quarter of an ounce of distilled snow-water was put into a small glass matrass, the neck of which was drawn out to the length of two feet, the water was boiled in it, and when

the atmospheric air was expelled, the orifice was closed. It was suspended over a lamp, and the water kept boiling for twelve days and nights; after it had boiled two days it became white, after six days it was like milk, and at the end of the twelfth day was quite thick : a powder subsided, from which the water was poured off; it was sensibly alkaline, from the alkali of the glass, and also held a portion of silex dissolved ; the deposite was siliceous earth. On breaking the matrass, the inner surface was dim and rough, as far as the boiling water had reached *. Lavoisier, by accurate experiments, proved likewise, that this is the source of the earth, which appears when water is boiled in glass vessels †.

Water exists in all crystallized salts, and in many of them in considerable proportion ; it seems to be essential to their crystalline form, but not otherwise to modify their properties. In the alkalis in their crystallized state, and in those acids too which assume a crystalline form, water of crystallization exists ; and this water probably exists as such, while what has been named their water of composition is in the state of its elements in simultaneous combination.

Water, at the temperature of ignition, affords oxygen to several of the metals; and at a natural temperature, aided by atmospheric air, it oxidates or corrodes the greater number of them. At a high temperature it is also decomposed by charcoal and sulphur, which receive from it oxygen.

Water is a solvent of many other substances. Few animal or vegetable products are insoluble in it, and all of them are affected by it as a chemical agent, receiving from it oxygen, or the re-action of their constituent principles being promoted by the fluidity it communicates.

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* Treatise on Air and Fire,—Preface.
† Mémoires de l'Acad. des Sciences, 1770, p. 397.

From the extensive solvent power of water, it is scarce-
ly ever met with pure in nature. Every kind of spring or
river water is impregnated with saline and earthy matter,
varying in its nature and quantity, according to the nature
of the strata over which it has passed. Spring water contains,
according to Bergman, a little carbonate of lime, muriate
of lime, and muriate of soda; river water contains carbo-
nate of lime, muriate of soda, and each of them also some-
times a little alkali *. There is a trace of magnesia to be
usually found in spring water, and frequently of sulphate
of potash and soda. In river water, the muriates, I have
found, generally to form the chief impregnation, while in
spring water the sulphates and carbonates are predomi-
nant, and in the former the alkalis are in larger quantity,
while the earths, particularly lime, exceed in the latter.
Well-water contains always sulphate of lime in consider-
able quantity, the presence of which is the cause of the
quality in waters termed *hardness*. Rain or snow water is
freer from these foreign substances, but is still not perfect-
ly pure. Rain water collected with every precaution, con-
tains, according to Margraaf, muriate of soda †, and ac-
cording to Bergman, muriate of lime. The presence of
these substances is judged of by the following tests, added
in the quantity of a few drops of each to an ounce or two
of water. A solution of nitrate of barytes produces a tur-
bid appearance from the presence of any sulphate or carbo-
nate, and the turbid appearance of it arising from the lat-
ter is removed on adding a drop or two of pure nitric acid.
A solution of nitrate of silver gives a bluish precipitate
from the presence of any muriate; and if this test is ap-
plied after the previous application of nitrate of barytes,
(care being taken that this last is free from all muriatic
acid,) it is more certain, as any precipitation from the pre-

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* Chemical Essays, vol. i, p. 192.
† Mémoires de l'Acad. des Sciences, 1770, p. 386.

sence of a sulphate or carbonate is removed.   A solution
of super-acetate of lead causes a turbid appearance, if sul-
phates or carbonates are present, while it produces a less
marked effect from the presence of muriates.   A solution
of oxalate of ammonia detects lime by precipitation ; and a
solution of soap in alkohol indicates, by the degree of tur-
bid appearance it produces, the predominance of sulphate
of lime. If a solution of phosphate of soda produce a milki-
ness after a previous addition of a similar quantity of car-
bonate of ammonia, magnesia is present. The presence of
free carbonic acid is detected by a slight milkiness being
produced by the addition of an equal portion of lime wa-
ter to the water, and with still more delicacy by super-
acetate of lead ; and it is discovered in the air expelled by
boiling.

Water is freed from these substances by distillation ;
and for any chemical process in which accuracy is requi-
site, distilled water must be used.

BOOK III.

OF ACIDS AND THEIR BASES.

Acids are among the most important of the chemical a-
gents; they act with much energy on a number of bodies,
and enter into an extensive series of combinations. The
greater number of them have been demonstrated to be
compounds, containing oxygen as a constituent element,
combined usually with inflammable bases. In conformity
to the arrangement I have adopted, the chemical history
of these bases is to be connected with that of the indiv-
idual acids. Some acids have compound bases of two or
more elements. These are formed by the processes of the
vegetable and animal systems; and being more strictly con-
nected in characters with vegetable and animal substances,
have usually been associated with them, an arrangement to
which I adhere.

The Acids are distinguished by the following general
properties.

They are sour to the taste. This property of sourness
belongs to no other bodies, and hence has been consider-
ed as synonymous with acidity. It is possessed by the dif-
ferent acids, however, in very different degrees; some of
them display it even when very largely diluted with water,
while in others it is scarcely apparent in their most con-
centrated state: these latter have at the same time in an
inferior degree the other acid powers. It appears to be
also connected with their corrosive quality in relation to

animal and vegetable matter; the stronger acids being highly corrosive, while the weaker have no such effect.

Acids change the blue, purple and green colours of vegetables to a red. This is one of their most obvious and distinctive properties; it belongs to the weakest of them; and hence it is considered even as the test by which a body is recognised to be acid. The more delicate vegetable colours, those of mallow, radish, violet, or litmus, are employed to discover it.

The acids have in general a strong attraction to water, and combine with it readily in every proportion without suffering any important modification of properties. In some of them it is supposed to exist in more intimate combination, and to be essential to their constitution in an insulated form. But this is a more doubtful opinion.

The relations of the acids to the alkalis and earths afford the most strict and distinctive character of acidity. They combine together with facility, and when in a certain definite proportion, which each has a tendency to observe, the properties of the acid, and those of the alkali or earth are mutually lost or neutralized. They also often combine in other proportions in which there is an excess of acid, or an excess of alkaline or earthy base; but still in these combinations, though the properties of one of the ingredients may be apparent, they are weakened to a certain extent. These compounds are denominated Salts.

The action of the acids on the metals gives rise ultimately to a similar result, but with an intermediate change, which affords another character by which they are distinguished,—that of imparting oxygen to the metal, or enabling it to attract oxygen from water which is present, or from atmospheric air. No acid combines directly with a metal, but all acids unite with the metallic oxides. Hence if an acid is presented to a metal, it often happens, from the tendency to this combination, that the acid suffers decomposition, oxygen is abstracted from a portion of it by

the metal, and the metallic oxide, as it is formed, combines
with the remaining acid.   Or if the acid is not decompo-
sed, it often enables the metal to attract oxygen from the
air, or from water present, and the same combination is
established.   As many of the compounds thus formed re-
main dissolved in the acid in a certain state of dilution, the
acids are said to dissolve the metals.   The same law is ob-
served as in the combination of the acids with the alkalis
and earths; in a certain proportion there is a mutual neu-
tralization of properties, and when combined in other pro-
portions, so that there is an excess of acid, or of metallic
oxide, the properties of the substance in excess are modi-
fied, and those of the acid are always so far impaired.
These compounds are named Metallic Salts.

These are the chemical agencies which are most cha-
racteristic of the acids, and which serve to define the class.
Any exceptions which have been stated with regard to
them are doubtful or unimportant.

The theory of the constitution of acids forms one of the
most important subjects of chemical investigation, as their
agencies are connected with an extensive series of combi-
nations and changes of composition, and indeed with near-
ly all the details of the science.   The earlier opinions on
this subject require no notice.   Lavoisier, by a very strict
and ample induction, established the general conclusion,
that acids are compounds of inflammable bases with oxy-
gen.   In the combination of oxygen with the simple in-
flammables,—sulphur, phosphorus, and carbon, the pro-
ducts are acids, when the full degree of oxygenation is e-
stablished ; from the same inflammable body, even differ-
ent acids are formed by its combination with oxygen in
different proportions ; in those acids, which have a com-
pound radical, or consist of more than one inflammable
substance, oxygen also exists ; and thus all acids, the com-
position of which was discovered by analysis, were found
to contain this element as a common principle.   From

analogy, it was inferred, that those few acids which had resisted the usual methods of decomposition, the muriatic, fluoric, and boracic, likewise contained it, and the general proposition was established, that Oxygen is the principle of Acidity.

Some facts, however, were known, which left some doubt with regard to the universality of this proposition. Berthollet had observed, that prussic acid, an acid of weak power, when decomposed by heat, gave no indications of oxygen in its composition. And he afterwards remarked, that the compound of sulphur and hydrogen, sulphuretted hydrogen, had the distinctive qualities of an acid, though containing no oxygen. The evidence, however, in support of Lavoisier's doctrine, that oxygen alone communicates acidity, appeared so strong, that these facts were regarded as still doubtful. The decomposition of prussic acid is a complicated process, affording several products from new combinations of its elements, and liable therefore to the fallacy, that a small portion of oxygen might escape observation. Hence Berthollet himself even continued to regard it as doubtful, whether oxygen existed in it or not. Oxygen was also supposed to exist in small quantity in sulphuretted hydrogen, and to give rise to its acidity.

The discovery of certain relations in another important chemical agent, at length led to other theoretical views. The substance named Oxymuriatic acid had been regarded as a compound of muriatic acid and oxygen. Gay-Lussac made the important experiment of submitting it, in its gaseous state, to the action of hydrogen gas, and ascertaining that muriatic acid gas is the sole product of this operation. This might be explained in conformity to the established doctrine, on the supposition, that the oxygen of the oxymuriatic acid combines with the hydrogen, and forms water, which the muriatic acid retains in combination in the gaseous state. But, as he also remarked,

oxymuriatic gas may be a simple substance, and, of course, from this experiment, muriatic acid may be inferred to be a compound of it with hydrogen. Sir H. Davy adopted this idea, and in conformity to it, he regarded oxymuriatic gas, or chlorine as he denominated it, as an acidifying element analogous to oxygen.

Gay-Lussac, prosecuting his investigations, established other important facts, and led to a different modification of these views. He discovered the radical of prussic acid, —a compound of carbon and nitrogen, and obtained it in an insulated form; and he found, that when combined with hydrogen, it forms prussic acid,—a result demonstrating that oxygen does not exist in the composition of that acid, and apparently proving that hydrogen is capable of communicating acidity. He farther found, that sulphuretted hydrogen contains no oxygen, but that by the most rigorous methods of determining its composition, it consists of sulphur and hydrogen alone; its acidity is unequivocal, and it affords therefore another example supporting the same conclusion. In conformity to this analogy, he considered hydrogen as exerting a similar agency in converting chlorine into muriatic acid. And the relations of a newly discovered substance, Iodine, farther confirmed this view. It was found to form an acid by combining with oxygen, and another acid by combining with hydrogen, and in this respect to be analogous to chlorine and sulphur. Thus all these results served to establish the conclusion, that hydrogen, as well as oxygen, produces acidity in their combinations.

Another class of facts had been established, important in relation to the theory of acidity, though not strictly conformable to any of the theoretical views hitherto explained. These I have next to state, and at some length, as they are the foundation of the opinion which I have already had occasion to remark has occurred to me on the constitution of acids.

These facts refer to the existence of combined water in acids, and the important influence it has in their acidity. In all the more powerful acids it exists in considerable quantity, nor can they be obtained free from it in a pure form. Its presence is discovered by its being obtained when the acid is combined with a base, and the quantity of it may be thus estimated. If sulphuric acid, for example, is combined with oxide of lead, a portion of water is obtained equal to about a fourth of its weight; and as the oxide of lead contains no water, it must be derived from the acid. If the same acid be combined with potash, it yields a similar quantity of water above that which the potash contains. With nitric acid, the result is perfectly similar, and the proportion of water is nearly the same. Muriatic acid, in its gaseous state, equally affords it in the same processes; and phosphoric acid, which bears being exposed to a red heat, still yields, when it is combined with a base after this operation, a quantity of water not less considerable. The same general fact is established by the circumstance, that these acids cannot be formed without the presence of water. In whatever manner sulphur and oxygen are combined, sulphurous acid gas is the product of their combination if water is excluded; and if water be admitted to a mixture of sulphurous acid and oxygen gas, they soon form sulphuric acid, while without water they do not unite. Nitric acid is equally incapable of being formed without the presence of water; and neither nitric acid nor muriatic acid, notwithstanding their volatility, can be expelled from those combinations in which they exist in their real state, without water be supplied. When the former is expelled from nitre by the action of sulphuric acid, the water of this acid is transferred to it; and when the nitre is heated with a dry acid, the nitric acid is only decomposed. And muriatic acid is not expelled from sea-salt, when submitted to the action of any decomposing substance, even at the most intense heat, if water is not

present; but if water be admitted, its expulsion is effected with the greatest facility. All these facts appear to demonstrate the existence of combined water in these acids in their insulated form *.

There are other facts which appear to prove that this water existing in acids has an important influence in their acidity. If phosphorus be burnt in oxymuriatic gas, or sulphur be combined with it, products are formed, which, there is reason to believe from the theory of the mutual action of these bodies, must consist of dry acids, and which at least contain the elements of acidity; they do not redden, however, litmus paper, the most delicate test of acids, if it is perfectly dry, but if it be moistened, it instantly receives a bright stain of red; and there is reason to believe that other acids, when free from water, do not exert this property of reddening the vegetable colours †.

Of these results, no satisfactory explanation could be given. It did not appear from any known agency of water, how it should be so essential to the constitution of these acids in their insulated form, or so materially modify their properties; it is, on the contrary, a substance in general weak in chemical energy, and producing few important changes in its combinations. They were, therefore, received merely as ultimate facts.

With regard to one of these acids, however, the muriatic acid, a different hypothesis, excluding this agency of water, had been proposed. It was considered, as I have already stated, as a compound of oxymuriatic acid or chlorine, and hydrogen; and the water obtained from it when it was combined with a metallic oxide, or any base containing oxygen, was considered not as pre-existing in it,

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* Gay-Lussac, Recherches, t. ii, p. 94, &c.
   Berthollet, Mémoires d'Arcueil, t. ii, p. 55, 60. &c.
   Philosophical Transactions, 1809, 1810.
† Davy, Philosophical Transactions, 1809, 1810.

but as being formed by the combination of this oxygen
with the hydrogen of the acid.   But while this view was
advanced with regard to this acid, the relation of water to
the other acids, according to the established doctrine, was
still admitted ; sulphuric, nitric, and phosphoric acids were
held to contain combined water ; and no better explana-
tion of its relation to them was given in this system than
in the other.   It therefore merely departed from analogy
in denying the existence of water in muriatic acid, a de-
parture more evident, since this acid resembles the others
so much in its powers, and displays an attraction to wa-
ter equally strong.

It was in prosecuting the discussion of this question,
and of the controversy which had arisen with regard to it,
that the view occurred to me which I have now to ex-
plain.

I had obtained water in various experiments from mu-
riatic acid gas, by methods in which the mode of account-
ing for it by the doctrine lately proposed could not be ap-
plied.   These I shall afterwards have to explain in illus-
trating the particular question with regard to the consti-
tution of this acid.   Such a result (supposing it to be ob-
tained) might be considered as establishing the conclusion,
that water pre-exists in this acid ; and a similar result with
regard to other acids had always been regarded as a proof
of the presence of water in their constitution.   It occurred
to me, however, that the conclusion is no necessary one in
any of these cases. When water is obtained from an acid,
it does not follow that this water pre-existed in it.   It is
possible that the elements only of water have existed in its
composition, and that in the chemical action in which wa-
ter is obtained, it is formed by their combination ; the o-
ther element, or elements, entering at the same time into
combination with the substance by which the change has
been effected.

According to this view, muriatic acid is a compound of

a radical at present unknown with oxygen and hydrogen; oxymuriatic acid is a compound of the same radical with oxygen; when it is converted into muriatic acid by the action of hydrogen, the hydrogen merely enters into the combination with the other elements; and when water is obtained from muriatic acid by the action of a base, it is owing to the base or its radical combining with the radical of the acid and a portion of its oxygen, while the hydrogen, with a portion of oxygen, combine and form the water obtained. Whenever this is admitted, the same view may be extended to other acids supposed to contain combined water. Sulphuric acid is not, as has been conceived, a compound of sulphur and oxygen, combined farther with a portion of water, but is a ternary compound of sulphur, oxygen, and hydrogen; and when water is obtained from it by the action of a base,— of oxide of lead for example, the result depends on its hydrogen and a portion of its oxygen combining, while the sulphur, which is the radical of the acid, the lead and the remaining oxygen enter also into combination. Nitric acid is in like manner a ternary compound of nitrogen, oxygen, and hydrogen: and phosphoric acid a ternary compound of phosphorus, oxygen, and hydrogen.

This is a conclusion equally probable *a priori* with that on which the common opinion rests. When water is obtained from a compound, it does not necessarily follow that it has pre-existed in it; or when it is communicated to a substance, it does not follow that it remains as water merely in combination. There are many cases of decomposition, in which it is known to be a product of the combination of its elements previously existing in a compound; and there are others in which, when it is communicated, it is known that it is resolved into its elements, which pass into new combinations. Nor is there any fact to oppose these conclusions in its relation to the constitution of the more powerful acids.

There is no principle on which the presence of this sup-
posed combined water can be accounted for.   That to
which it must be ascribed is the attraction of the acid to
water.   But it bears no relation to this, for there are
acids having a strong attraction to water, such as the sul-
phurous, which contain none.   The elements of water,
therefore, exist in the composition of those acids which
afford it, and it is formed in those cases of chemical action
in which it is obtained : those which do not contain these
elements afford none.

The view itself accords much better with the phenomena
than the opposite conclusion.   On no principle can it be
inferred, that water should increase acidity, nor can it be
explained how it should have such an effect.   But how
oxygen and hydrogen should produce it by their joint
operation is sufficiently apparent, since each of them se-
parately does so.   It accordingly appears, that their uni-
ted action on the same base gives rise to a higher degree
of acid power.   Sulphur with hydrogen forms a weak acid ;
with oxygen it forms another acid not distinguished by
much energy of action ; but with both oxygen and hydro-
gen it forms an acid of the greatest strength.

It will be found also to accord with the law of definite
proportions.   Considering the combined water, as it is
called, in the acids, as existing in the state of its elements,
the quantity is such, that the proportions will be found
conformable to the known relations of these elements in
their combining quantities to the radical of the acid ; as I
shall have to shew under their individual history.   And
hence it follows, as by far the most probable conclusion,
that these elements are not in the state of water, but are
in direct combination with that radical.

Lastly, this doctrine affords a more satisfactory view
than any other of the question which has been so much
the subject of discussion,—the relations of muriatic and

oxymuriatic acid. This I shall afterwards have to explain.

On the general theory of acidity, then, it may be inferred, conformable to the induction of Lavoisier, that oxygen communicates this property to many of the combinations into which it enters. It is also established, conformable to the views of Berthollet, and the discoveries of Gay-Lussac, in the examples of sulphur and cyanogen, that hydrogen produces the same effect. And if the view I have stated be just, the farther induction will fall to be admitted, that the joint operation of these elements gives rise to a similar result, and that they enter into the constitution of the more powerful acids. Some have maintained, that acidity is not to be regarded as connected peculiarly with any principle, but as depending merely on some mode of combination, or as capable even of being exerted by a simple substance. But the generalization which evidently exists on this subject is not to be neglected. When a number of bodies agree in the possession of certain common properties, and when it is farther found, that in the chemical constitution of these bodies a common element exists, united in each with a particular base, it is with justice inferred, that their generic properties depend more particularly on the agency of this principle. On these grounds, Lavoisier established the induction, that oxygen is the principle of acidity; and, on the same grounds, the farther inductions which have been established rest. At the same time, it is not improbable, conformable to a view which I have formerly illustrated, (System, 3d edition, vol. ii, p. 316.) that acidity may be a property depending on the base of acids, and that it is only developed, or brought into action by these acidifying elements.

More than one acid, it has been stated, may be formed from the same radical: thus sulphurous and sulphuric acids are derived from sulphur, nitrous and nitric acids from nitrogen, phosphorous and phosphoric acids from

phosphorus. These have been supposed to be formed merely from different proportions of oxygen; but this is doubtful, those at the higher degree of oxygenation contain combined water, according to the common hypothesis, in other words, they are ternary compounds of the radical with oxygen and hydrogen, and it is uncertain, if in any case two binary acids can be obtained insulated from the same radical. Carbon has been supposed to form only one acid, that in which it is saturated with oxygen; but there is reason to believe that it is analogous to the others, and that even different acids are formed from it by the united action of oxygen and hydrogen in different proportions : such are the oxalic, tartaric, and others.

Acidity may be inferred to be more dependent on the base, than on the degree of oxygenation, from the fact, that an acid, at a low degree of oxygenation, saturates as much of an alkali, as when the proportion of oxygen is increased, the radical being the same ; sulphurous acid, for example, when combined with an alkaline base, forming a salt, which, by absorption of oxygen, passes into a different salt, in which, however, the acidity is not augmented, but the state of neutralization remains unchanged. This conclusion follows from this fact, so far as the power of neutralizing alkalinity is considered as the test of acid energy; though, taking the other acid properties into account, they are evidently augmented by the higher proportion of oxygen, and the addition of hydrogen. And neutralization is probably to be considered not as the effect of an acid weakening the properties of an alkali, but of subversion of composition, arising from affinities exerted between the radical of the acid and that of the alkali, and hence dependent on their relations.

The view I have illustrated with regard to the constitution of acids may be extended also to that of the alkalis and earths. As oxygen is an element conferring acidity, so in other examples it communicates alkalinity. Hydro-

gen, it can be shewn, has the same effects. And the one property, as well as the other, seems to be produced in a higher degree by their joint action, than by either alone. This farther leads to a view of the compounds which these form with the acids, different from what has been received. This I shall immediately have to illustrate. Instead of stating the arguments in support of these doctrines at more length, I conceive it will be more satisfactory to give the original Memoirs in which they were announced, as they can thus be delivered in connection, and with those proofs and illustrations which cannot with propriety be given in this part of the work. I shall add these Memoirs, therefore, as an Appendix to this volume. At the same time, I shall apply the view to the individual substances, in delivering their history.

THE acids combine with the Alkalis, Earths, and Metallic Oxides. These combinations form an extensive, and a very important order of chemical compounds; and some general facts require to be stated with regard to them, which have properly a place under this division of the classification.

When an acid is added to an alkaline base, its acidity is impaired proportional to the quantity of alkali present, and, conversely, the alkalinity of the base is weakened by its combination with the acid. There is a certain stage in the combination, in other words, a certain proportion in which the two bodies have combined, in which the properties of neither are apparent, but are mutually neutralized or lost. The compound has neither the sour taste of the acid, nor the acrid taste of the alkali; it has the causticity of neither, and it does not affect the most delicate vegetable colours. This, in chemical language, is denom-

inated Neutralization, and the compound is named a
NEUTRAL SALT.

These effects are displayed when the two bodies are in
a state of solution, and, in this case, while the compound
remains dissolved, the acid and alkali appear to unite in
all proportions, each weakening the other according to its
energy and quantity. But when the compound is obtain-
ed solid by evaporation of the solvent, or when, from its
insolubility, it is precipitated as it is formed, it is establish-
ed in more definite proportions.

In general, it is thus obtained by crystallization or pre-
cipitation in the neutral state. This is not always the
case, however; it sometimes separates, and is obtained in-
sulated either with an excess of acid, or an excess of base.
Some acids, in combining with bases, form only neutral
compounds, such as the nitric; some have a tendency to
form compounds with excess of acid; such are the sul-
phuric, the oxalic, or the tartaric; and in some, as in the
carbonic or the boracic, the tendency is to establish in-
sulated combinations having excess of base. And where
compounds are formed with either excess, neutral com-
pounds, from the same substances, can also be obtained.

The important law has already been stated with regard
to saline compounds, (vol. i, p. 123.) in common with o-
ther combinations established in definite proportions, that
where the same ingredients are combined in more than
one proportion, a simple arithmetical ratio exists between
the two proportions of one of the ingredients, the higher
proportion being double that of the lower. Potash, for
example, combines with carbonic acid in two proportions;
one in which there is an excess of base, and another which
is analogous to the neutral compound, in which the quan-
tity of carbonic acid is twice the quantity in the former.
With soda it is the same. Sulphuric acid, in like man-
ner, forms two compounds with potash, one neutral, and
one with an excess of acid, and the quantity of it com-

bined with a given weight of potash in the latter, is twice the quantity of that combined with the same weight of potash in the other. The same law is observed in the combinations of oxalic acid with potash, and with strontites; and there is reason to believe that it operates in all saline compounds where different proportions exist.

Berthollet, from his general views of chemical attraction, (already explained vol. i, p. 131.) advanced the opinion, that the determination of the proportions of the elements in saline compounds depends principally on the force of cohesion exerted in the process of crystallization or precipitation. An acid and an alkali, he supposed, are disposed to combine in every proportion, each weakening the properties of the other, in proportion to the quantity of it in the combination; there is therefore one proportion in which these opposing properties must be neutralized; but in all the others, there are equal indications of chemical union. The force of cohesion determines the separation of the compound from the fluid in which it is formed, and thus apparently gives rise to a fixed or determinate proportion being observed. But when this does not happen, there is no interruption of the progress of the combination, and it therefore takes place in every proportion. This separation will always happen where the tendency to cohesion is greatest; it coincides sometimes with the point of neutralization; sometimes not. That it should be at the point of neutralization, seems to follow, from this being the point at which the elements of the compound exert their respective energies with greatest power, and where therefore the condensation is greatest; it may deviate from it, however, especially where one of the elements has a greater tendency to solidity than the other, the compound separating with an excess of that ingredient; and sometimes both the neutral compound, and that with an excess, may be obtained by peculiar arrange-

ments of those circumstances which influence chemical attraction.

Berthollet gives some facts which accord with those views. The combinations, for example, of tartaric acid, or of oxalic acid with the alkalis, are disposed to crystallize with an excess of acid, which is accounted for on the principle, that the acid in these cases is the ingredient most disposed to crystallize. And the principle of his theory cannot be denied, that the influence of cohesion may insulate a compound at a particular stage of combination, and give rise to a fixed proportion of its elements. There are other facts, however, in opposition to the doctrine. In the combinations, for example, of phosphoric acid or boracic acid with an alkali, such as soda, the compound becomes insulated with an excess of base, though the acid is the ingredient on which the force of cohesion operates with greatest effect, and which also, from its inferior solubility, is most disposed to pass into the solid form. The general law, too, of chemical attraction, is to establish compounds in definite proportions ; and the peculiar law connected with this, that where two bodies combine in more than one definite proportion, the higher proportion of one of them is a simple multiple of the other which exists in these combinations, proves that the determination of these proportions does not depend on external forces, but on the immediate exertion of chemical attraction ; for, as has been remarked, (vol. i, p. 135.) such a result cannot be accounted for from the influence of these forces, but must arise from the mutual attraction being exerted with more force in certain relative quantities of the bodies than in others. Lastly, the relation of combining or equivalent quantities in the elements of saline compounds exists in their combinations, and proves that the proportions of these are determined by the operation of chemical attraction.

These facts, therefore, appear sufficiently to establish

the law with regard to saline compounds, which exists in general in chemical combinations, that their elements combine in certain definite proportions. In general the combination is established in that proportion in which the acid and base are neutralized; and where it exists with an excess of either, that excess has a simple arithmetical ratio to the quantity of the same ingredient in the smaller proportion. At the same time, some difficulties remain with regard to this, which have been already stated in the illustration of the general doctrines of Chemical Attraction, as drawn from saline compounds. Berthollet has shewn, that even in those cases in which this law can be traced, such as those from which it was inferred by Dr Wollaston, although two definite compounds conformable to it exist, intermediate compounds can be formed and obtained crystallized, and compounds with smaller proportions of one of the ingredients can also be obtained, (vol. i, p. 135-145.) And the influence of cohesion in regulating the proportions cannot be altogether denied, since in general we find them to be established in those which form the least soluble compounds. Definite proportions, at least more numerous than has been supposed, must probably be admitted to exist: and the relation of the force of cohesion to the exertion of chemical attraction is a subject which still remains to be elucidated.

The relation of the acids to the earths and the metallic oxides is precisely similar to that to the alkalis. They combine together so as to form neutral compounds; and they frequently also unite in other proportions, so as to form compounds with excess of acid or excess of base.

An acid is frequently capable of being combined with two bases, so as to form definite compounds: sometimes two alkalis are thus present together, or an alkali and an earth, or an alkali and a metallic oxide; and these ternary salts, as they are named, may be either neutral or otherwise. The law has already been pointed out, (vol. i,

p. 159,) that in these compounds the relation of the acids in saturating the two bases is the same as that which it would observe in their separate state, according to their respective quantities, so that a neutral ternary compound may be resolved into the two neutral binary compounds formed by the combination of the acid with each base; and a ternary compound with excess of acid, or of base, is in like manner capable of being resolved into the binary compounds with a similar excess. Hence, such combinations may be represented as consisting of the two binary compounds, though it is probable that this is not their constitution, but that the three elements are in simultaneous combination.

The acids differ greatly in their power of neutralizing the alkalis and earths, very different relative quantities being requisite to produce the effect; and conversely, the alkalis and earths differ as much in their power of neutralizing the acids. According to the view given by Berthollet, already explained, the energy of the affinities of the acids to the salifiable bases is indicated by their relative powers of producing this neutralization, comparing them in the same weights; as the affinities of these bases to the acids may in like manner be judged of from their power of neutralizing them,—the less of any of these substances, whether acid on the one hand, or base on the other, which is required to neutralize a given quantity of another of the opposite order, the stronger being its attraction towards it. Of the acids the carbonic acid is on this principle superior to others, next the muriatic, the oxalic, sulphuric, and nitric. Of the bases, ammonia is superior, next to it is magnesia, then lime, soda, potash, strontites and barytes. And the deviation of the order of decomposition from this order in each is to be ascribed to the influence of the external forces which modify chemical attraction. The numbers attached to them in Dr Wollaston's scale denote the quantities necessary to produce re-

ciprocal saturation, and represent their comparative neu-
tralizing powers.

One of the most important problems in chemistry, is
that of determining with precision the composition of salts
with regard to the proportions of their constituent parts.
It is so, in the theory of the science, as connected with the
doctrines of attraction ; and it is not less necessary in prac-
tical chemistry, as abridging the labour of analysis, and
securing that exemption from discordant results, which
would be unavoidable in experiments so delicate when
made by different individuals.

The mode of determination usually employed is to com-
bine a given weight of a base with as much acid as produ-
ces neutralization, or conversely, to saturate a given weight
of an acid by the requisite addition of base, and then to
ascertain the weight of the solid salt formed by obtaining
it by evaporation, and the necessary exposure to heat in a
dry state.   Or sometimes the composition may be disco-
vered by analysis,—decomposing a given weight of a salt
by the addition of a substance which combines either with
the acid or base, and forms a compound which can be
easily obtained insulated, and the precise composition of
which is previously known.

By the first of these methods, Bergman, and afterwards
Wenzel, found the composition of a great number of salts.
The investigation of this, however, is attended with much
difficulty, principally from the presence of water.   Were
the ingredients obtained insulated, and did the compound
retain no water when dried, the above method would give
accurate results.   But the reverse is the case.   Both the
acids and bases are liable to contain water, and some of
them (according to the common expression of the fact)
cannot be procured free from it ; many of the salts also
retain it with great force ; they are either unable to bear a
degree of heat sufficient to expel it, or there remains an
uncertainty whether it is entirely expelled.   Hence, many

of the results in which these circumstances were present, and not sufficiently attended to, were necessarily incorrect.

The acids, more particularly, were known to contain combined water in the strongest state of concentration in which they can be procured ; and it became, therefore, a leading object to discover the quantity of this, or to determine in each case what constitutes the real acid.   Mr Kirwan entered on this investigation, and prosecuted it at much length.   His early researches * were imperfect, principally from being connected with two assumptions, neither of which is just ;—one, that muriatic acid in its gaseous state may be considered as real acid, and the other, that the same quantity of real acid will always be requisite to saturate an alkaline base ; and hence, from the quantity of muriatic acid necessary for this, the quantity of real acid in the others might be inferred.   He afterwards corrected these, and founded his results on the general principle, that the acid which remains in a compound salt, after exposure to the highest heat it can sustain, generally a red heat, is real acid.   The sulphuric acid in sulphate of potash, the nitric acid in nitrate of potash, and the muriatic acid in muriate of potash, strongly heated, he considered as real acids   From finding the quantities of these acids of a certain specific gravity, which entered into the composition of a given weight of these salts in this state, he inferred the quantity of real acid which, in their usual state of concentration, they contain.   And by discovering the quantities of them which the different bases required for saturation, he discovered their proportions in the salts†. The tables representing these have been already inserted, vol. i, p. 193.

Admitting even the principle on which the determina-

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* Philosophical Transactions, vol. lxxi, lxxii, lxxiii.

† Transactions of the Irish Academy, vol. iv. and vii.

tion rests, that the acid found in the method of Kirwan is real acid, his results are still liable to error, principally perhaps, as Berthollet has remarked *, from the imperfect method which he employed of determining the quantity of salt formed, not by its actual weight, but by the quantity of acid of a certain specific gravity, and containing, according to the preceding assumption, a certain quantity of real acid, which a given weight of base was found to saturate, and partly also from there being no principle to detect the slighter inaccuracies of experiment. His determinations are, accordingly, in many cases, incorrect.

In the analyses which have been since executed, the same principle is adopted, that the real acid is that existing in a salt after exposure to a heat sufficient, it is supposed, to expel all water, usually a heat of ignition. The quantity of salt formed, from a given weight of base, is found by evaporation and exposure of the dry product to a red heat, if it can sustain this without decomposition ; the weight gained by the base denotes the quantity of acid, and in a crystallized salt, the quantity of water of crystallization is at the same time usually found, by ascertaining the loss of weight it sustains in exsiccation from its crystallized form : And by improved methods of experiment, more accurate results perhaps are obtained.

The progress of the science, too, and in particular the discovery of the relation in the combining quantities of bodies, has introduced more facility and more certainty into these researches. The first view, in fact, of this relation, it has already been remarked, (vol. i, p. 137.) was in the investigation of the saline compounds in a principle discovered by Richter, and applied by him to determine their composition, or at least to verify the results on which this is assigned.

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* Chemical Statics, vol. i, p. 32.

Richter observed, that when two neutral salts which produce double decomposition are mixed together, the state of neutralization is preserved; that is, the two new salts which are formed are equally neutral with those that had been decomposed. And it occurred to him, that this afforded a mode of verification by which the accuracy of the proportions in saline compounds might be ascertained; for, from the proportions assigned, we discover what quantity of acid and what quantity of base, in each of the salts decomposed, produce the state of neutralization in them; and, in like manner, from the proportions assigned, we discover what quantity of acid and of base are required to establish the same state in the salts that are formed. We discover, therefore, whether in the original salts there is that quantity of each acid requisite to saturate each of the bases in the new salts when the state of combination is changed, or whether there is more or less, and, of course, whether the compounds ought to be neutral, or have an excess of acid or base. If the actual result corresponds with that which must follow from these proportions, it may be inferred that they are truly determined; if not, the estimate in the proportions in one or more of the salts must be incorrect.

Richter, on applying this mode of verification to the proportions assigned by Kirwan, found them inaccurate. In the decomposition, for example, of muriate of lime by sulphate of potash, there ought, from the numbers, to be an excess of alkali, while the result is perfect neutralization. And he farther found, that the results by Bergman and Wenzel were equally incapable of standing this test. An example from Kirwan's tables will illustrate this more clearly.

Muriate of magnesia and sulphate of soda produce mutual decomposition, and form compounds which are neutral. The following are the proportions of acid and base

requisite for neutralization in these salts, and in those which they form :

Sulphate of magnesia,	100 of acid,	56.6 of magnesia.
Sulphate of soda,	100 of acid,	70 of soda.
Muriate of soda,	100 of acid,	68.5 of soda.
Muriate of magnesia,	100 of acid,	46.3 of magnesia.

The muriate of magnesia consists of 100 of acid, and 46.3 of magnesia. This quantity of magnesia, in combining with sulphuric acid, requires 81.802 of that acid; for sulphate of magnesia, according to the table, consists of 56.6 of magnesia and 100 of acid, and 46.3 is to 81.802 as 56.6 is to 100. But if the magnesia in this new combination abstract only 81.802 of sulphuric acid, no more than 57.261 of soda will be set at liberty, this being in the relation of 100 of acid to 70 of base in the sulphate of soda. Now it appears from the table, that 68.5 of soda are necessary to saturate 100 of muriatic acid; but as there is only liberated 57.26, a quantity capable of neutralizing 83.892 parts, there must remain from the decomposition of the muriate of magnesia 16.408 unsaturated, which ought to communicate acidity to the mixture. The mixture is however found, on making the experiment, to remain neutral, and therefore the proportions in some, or perhaps in all of these salts, must be wrong. These numbers are from Kirwan's earlier tables, but similar results are obtained from the corrected numbers in his last table, as Berthollet has shewn by several examples *.

Richter, in prosecution of these researches, executed an extensive series of experiments, in which he constructed tables representing the quantities of the different bases, necessary to saturate 100 parts of each of the principal acids. From these it appeared, that the bases observe the same order with regard to all the acids,—alumina being

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* Chemical Statics, vol. i, p. 86.

the one with regard to all of them, the smallest quantity
of which neutralizes a given weight of acid, magnesia be-
ing next to it, and requiring a larger quantity, and barytes
being the one the largest quantity of which is requisite to
produce neutralization : and he farther found, that the
same proportion even exists between them in relation to
all the acids in their neutralizing power. The same law
holds with regard to the acids, as applied to the respec-
tive bases. Fischer made the important observation, that
the tables of Richter might be comprised in one table,
and numbers applied to each acid and base denoting
their relative neutralizing powers. This table has been al-
ready explained, and a place given to it (vol. i, p. 137. 193.)
as interesting in the history of the investigation, though the
numbers are not accurate.

The principle must be apparent on which the impor-
tant fact observed by Richter is founded, that the state of
neutralization in the mutual decomposition of saline com-
pounds remains unchanged. Such is the relation of acids
and bases, that the same proportional weights of the dif-
ferent acids which one base neutralizes are neutralized
by all other bases; and, conversely, the same proportional
weights of the different bases which one acid neutralizes
are neutralized by other acids. Hence, if the proportions
of two compound salts are so adjusted, that the quantity
of acid combined with the base in the one shall be such
as to neutralize the quantity of base in the other, the quan-
tity of acid with which that base is combined will equally
neutralize the base of the first. If these two salts, there-
fore, produce mutual decomposition, the state of neutra-
lization must remain, excluding the formation of super- or
sub-salts.

It is obvious that this is merely the general law of combin-
ing or equivalent quantities, applied to the elements of sa-
line compounds. Every acid has a certain equivalent pro-

portion to others in which it combines with those bodies
to which it exerts an attraction, that is, to the different
bases.   Each base has in like manner a certain equiva-
lent proportion to the others, in which it combines with
the acids.   And the extension of the law to other bodies
has merely reduced these to the more general standard
to which the combining weights are referred.   They are
accordingly referred in Dr Wollaston's scale to oxygen
as 10.

By the application of this principle, much more accu-
racy is given to the determination of the composition of
saline compounds, both as it facilitates the investigation,
by admitting of the application of analytic methods, in
which one acid or one base is substituted for another in a
combination, and the result established by means of the
equivalent weights, and as it affords a check on the errors
to which experimental processes are liable.   By being far-
ther connected with the same relation of equivalent quan-
tities in the more remote elements of these compounds,
additional certainty is given, for the connection of the one
with the other could not be established to any extent if
any important error existed.   It is from this consideration
that more confidence may now be given to the conclusions
on this subject, as otherwise the direct experimental re-
sults would always leave uncertainties, more especially
from the difficulty of determining whether water was en-
tirely excluded.   The discovery in this point of view may
be considered perhaps as the most important ever made in
chemistry.

One other principle has been pointed out as applied to
the determination of the composition of saline compounds,
that suggested by Gay-Lussac from the relation subsisting
between the acid in a salt, and the oxygen in the oxide
which is its base,— the quantity of acid in the salt (when
neutral) being proportional to the quantity of oxygen in

the base * ; hence, if the proportion of oxygen to the metal be found, which may be done by methods unconnected with the usual modes of investigation, the quantity of acid, and of course the quantity of base may be inferred. The principle is established from the fact, that when a metallic salt is decomposed by the action of another metal abstracting both its oxygen and acid, the state of neutralization is preserved, the metal producing the decomposition, taking the oxygen of the other, and the quantity of oxide thus formed neutralizing the quantity of acid which the former oxide neutralized ; the acid therefore is proportional to the oxygen, and the only change is in the substitution of the metal.   This fact had been before announced by Richter, and he had inferred from it, that " different metallic oxides, saturating a given portion of an acid, contain the same quantity of oxygen." It equally follows, that different oxides containing the same quantity of oxygen saturate the same quantity of acid : and as the fixed alkalis and the earths are, strictly speaking, metallic oxides, the principle may be applied to all neutral salts, with the exception of those having ammonia for their base.   Berzelius has accordingly employed it to determine the proportion of acid and of oxide in a number of salts †.

THE doctrine which I have explained of the chemical constitution of the acids, with the corresponding doctrine as applied to the alkalis, leads to a view of the constitution of the compound salts very different from that which has

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* Mémoires d'Arcueil, t. ii. p. 159.
† Nicholson's Journal, vol. xxx, p. 272.

been hitherto received, and which I have now illustrated. They probably contain neither acid nor base, but are ternary compounds of the inflammable radical of the acid, and the metallic radical of the base, with oxygen.

When a neutral salt is formed by the reciprocal action of an acid and alkali, if the acid is a ternary one, such as the sulphuric, composed of a radical, sulphur, with oxygen and hydrogen, it does not merely combine with the base, but its composition is subverted, and its hydrogen with a correspondent portion of oxygen combine, forming water. Now there is no proof that the radical of the acid combines with the remaining oxygen to form a binary compound, (corresponding to the real acid of the common doctrine) which unites with the base. And, in like manner, when a base of ternary composition, potash, for example, is acted on by an acid, it does not directly combine with it, but is decomposed, its hydrogen with a portion of its oxygen forming water ; and there is the same deficiency in this as in the other case, of the radical of the alkali, the potassium, combining with the remaining oxygen to form a binary compound, (real potash as it is hypothetically termed,) which unites with the acid. In all these cases the two radicals, that of the acid and that of the base, may enter with the remaining oxygen into simultaneous combination, and the neutral salt be of course a ternary compound of these elements. This is rendered probable from the consideration that the changes seem to arise from the mutual affinity of the two radicals, and the affinity of the hydrogen to the oxygen, while there is no proof whatever of the opposite opinion : and it is still farther confirmed by the fact illustrated in the memoirs to which I have already alluded, annexed to this volume, that the relations in proportions are conformable to those of the ultimate elements in the compound.

When a binary acid, such as the sulphurous, acts on a base, or when a base of binary composition, such as a

metallic oxide, acts on an acid, analogy leads to a similar conclusion, that a ternary compound is established.

Neutralization has been considered as the loss of distinctive properties, from the action of two bodies of opposite characters. According to the present view, it is the entire subversion of composition, and the formation of a compound, in which the elements are quiescent. The proportions are established conformable to the relative combining weights which these observe. The oxygen is in one of the definite proportions in which it combines with the radical of the acid, and the radical of the acid and of the base are in their definite proportions to each other.

As the formation of compound salts thus depends on relations of their ultimate elements, their decomposition depends on similar relations. When sulphate of potash is decomposed by barytes, barium takes the place of potassium, and enters into combination in the definite proportion which it observes to sulphur, while the same definite proportion of oxygen to sulphur remains. In the double decomposition of sulphate of potash by nitrate of barytes there is the exchange of barium to sulphur and oxygen, and of potassium to nitrogen and oxygen. The quantities in these combinations must be equivalent to each other, and therefore the state of neutralization must remain. The capacity of saturation in the different bases to the acids, and in the different acids to the bases, will depend on the same relations of the ultimate elements,—a larger quantity, for example, of barytes, than of potash is necessary to saturate a given weight of sulphuric acid, because a larger proportion of barium than of potassium combines with sulphur. Hence all these results will be found conformable to the laws which have been stated above; according to the established doctrine.

Though I have thought it necessary to illustrate these views, I shall, under the history of the individual salts,

state their composition in the usual manner. The assumption of real acid and real base is in general hypothetical, but the composition can at least be always represented under that hypothesis ; and it might be too great an innovation at present to employ terms suggested by the opposite theory, nor will it be necessary to bring it forward under each example.

The NEUTRAL SALTS, as an Order, have certain common properties which it is necessary to state, independent of their particular description. The properties of the base and of the acid, it has already been stated, are mutually lost. To a certain extent, however, they can sometimes be traced, more especially to the base, so far, that certain qualities belong to the salts which it forms ; all the ammoniacal salts, for example, being volatile, a property probably derived from the ammonia, those of magnesia being bitter, of alumina styptic, and of glucine sweet. Properties derived from the acid are less apparent, except such as are connected with the decomposition of the salt, and the agency of the acid itself. As genera, they may be connected either with the acid or with the base. Their generic characters, in the first point of view, I shall state under the history of each acid ; those in the second, under the history of the respective bases : And, with the last also, according to the arrangement I have adopted, I enumerate the individual species.

The neutral salts are in general soluble in water, but to this there are many exceptions, and they differ much in the degree of solubility. Some have so strong an attraction to that fluid, that they require to be exposed to a strong heat to obtain them solid ; some dissolve in half their weight of water, some require an equal weight, double, or more, others take 1000 or 2000 times their weight. Chemists have agreed to term those salts Insoluble, which require for their solution more than 1000 times their weight

of water. The solution of salts in water is accompanied
with a change of temperature, generally a diminution, and
that sometimes considerable, owing to the enlargement of
capacity attending the solution, from the transition of the
solid salt to the fluid form.

The solution of salts is usually promoted by an increase
of temperature; but in different salts the increased solubi-
lity from this cause is very different; while there are some
sea-salt, for example, which dissolve as abundantly in cold
as in boiling water. This difference depends on their re-
lative forces of cohesion; those which have their cohesion
most weakened by a given temperature, in other words,
which are fusible with the least heat, having their solubi-
lity in water most augmented with increase of temperature.
A table of the solubility of salts will be found at the end
of the Chapter.

When a salt has been dissolved in water, it may be re-
covered by evaporation of the water, and it will appear in
a regular or irregular figure, according as the evaporation
is conducted. If it is not carried too far, so that cohesion
is forcibly and irregularly exerted, producing merely ag-
gregation of the particles, it consolidates on cooling in
crystals more or less regular. This susceptibility of cry-
stallization is a distinguishing property of salts, since the
greater number possess it, and it is more remarkable in
them than in other bodies. In different salts the figure of
the crystals is very different, and it is also liable to be va-
ried by circumstances. In some cases regular crystals can-
not be obtained by hasty evaporation; but by slow and
spontaneous evaporation, crystals are obtained even more
regular in their figure, and denser in their texture than
those that are otherwise formed.

When salts are crystallized, they retain a quantity of wa-
ter which is essential to the constitution of the crystal.
This quantity is very different in different salts; in some
it exceeds the weight of real salt, in others it is not above

two or three in 100 parts.   From the results of the re-
searches of Berzelius, it is doubtful if it can be brought
under any regular law.   If more than one salt is in solu-
tion, they crystallize apart from their different degrees of
solubility, but the crystals of each appear to retain, me-
chanically lodged in them, a portion of the mother liquor,
as the residual solution is named, and hence are not ob-
tained perfectly pure ; they are only rendered so by re-
peated crystallization ; the small quantity of foreign mat-
ter becoming at length evanescent.   Several characters
which distinguish the salts depend on their water of cry-
stallization.   Thus some, when exposed to a moderate heat,
fuse, but if the heat be continued, become again solid ; this
is termed the Watery Fusion of Salts ; it takes place in
those which contain a large quantity of water of crystal-
lization, and is owing to the heat enabling the water to
dissolve the salt ; when this water is evaporated, the solid
salt is left, and may be made to undergo a real fusion, by
giving it the necessary increase of temperature.   Other
salts when exposed to heat are quickly split, with a crack-
ling noise.   This is termed Decrepitation ; it takes place
in those which have little water of crystallization, the in-
creased temperature converting it into vapour, by which
the crystals are suddenly burst.   Some salts when in cry-
stals lose their transparency by exposure to the air, are
covered with a white crust, and at last fall entirely into
powder.   This is termed Efflorescence ; it depends on the
abstraction of their water of crystallization by the attrac-
tion exerted to it by the atmospheric air.   There are others
that have so strong an attraction to water, that they ab-
sorb it from the atmosphere, and soon become fluid. This
is termed Deliquescence, and such salts are named Deli-
quescent.

    Insoluble salts, which are incapable of crystallizing, and
which appear to have no affinity to water, were supposed
to retain none, when freed from humidity by drying. This,

however, is not the case.   If any salt might be supposed to be free from water, it is sulphate of barytes, for it is perfectly insoluble.   Yet Berthollet found, that after being exposed to the most intense heat of a forge it contains water, as when mixed with iron-filings and exposed to heat in an earthen retort it afforded a large quantity of hydrogen gas.   The same result was obtained with sulphate of lime.   And when Berthollet endeavoured to expel all the water from salts known to contain it, by intense heat, he found this impracticable; muriate of lime, for example, after it had been subjected to the most violent heat in a forge, giving a large quantity of gas when heated with iron-filings.   It cannot therefore be affirmed, as Berthollet remarks, that a salt is ever obtained free from water; nor can the quantity be estimated, for even iron may be unable to effect the decomposition of the whole, the last portion being retained by an affinity sufficiently powerful to preserve its constitution *.   This presents some difficulty with regard to the theory of the determination of the composition of salts, which, as it is at present assigned, involves the conclusion that the salts are obtained free from water.

It remains to explain the nomenclature of the acids and of the compound salts.   This, as framed by Lavoisier and his associates, was systematic and precise, and the substitution of it, in place of the arbitrary and unconnected nomenclature formerly in use, was an important benefit conferred on chemistry.   Yet it also affords a proof of the evils attached to a theoretical nomenclature, even when the theory on which it is founded appears to be just; for unquestionably much of it is now exceptionable, the terms involving opinions which are not only doubtful, but some of them false; and the system not being adapted to ex-

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* Mémoires d'Arcueil, tom. ii, p. 63, 64.

press other results which the progress of the science has established.

Acids are compounds of oxygen with certain bases. The name of each acid, therefore, is derived from the base of which it is formed. But as this base is often capable of combining with two proportions of oxygen, and thus forming two different acids, these must be distinguished. This was done by a variation in the termination of the name, the syllable *ic* being the final one, in the name of the acid which contains the larger proportion of oxygen, and that of *ous* where it contains the smaller proportion. Thus sulphur, with oxygen in two proportions, forms two acids ; the word Sulphur is the radical whence their names are derived ; the one, that with the smaller proportion of oxygen, is the Sulphurous Acid ; the other, the Sulphuric. We have thus also the Phosphorous and the Phosphoric, the Nitrous and Nitric, &c.

Where the base gives rise to only one acid, the name terminates in *ic*, as in the example Carbonic Acid. The acids belonging to the vegetable and animal kingdoms have a compound base, from which the name cannot be derived ; it is taken, therefore, from the substance from which they are formed or prepared, as the Citric, Malic, &c.

The nomenclature of the salts, formed by the union of the acids with the alkalis, earths, and metallic oxides, is equally systematic. All the salts which are formed from one acid, are considered as forming a genus, under which are placed as species the individual salts, formed by the union of that acid with these different bases. The generic name is derived, therefore, from the name of the acid ; the specific name from that of the base. When the name of the acid of which the salt is composed is that which terminates in *ic*, the final syllable of the name of the salt is *ate ;* when, again, the name of the acid terminates in *ous*, that of the salt formed from it has the last syllable *ite*. Thus, all the salts formed from sulphuric acid constitute

a genus to which the name Sulphate is applied, and the species are designated by the addition of the name of the base, as Sulphate of Soda, Sulphate of Lime, Sulphate of Iron. Those, again, formed by the sulphurous acid, are named Sulphites, as Sulphite of Ammonia, &c. On the same principle, we have Nitrates and Nitrites, Phosphates and Phosphites, Muriates, Carbonates, &c.

Salts are formed with an excess of acid or of base; to denote these, the mode employed by the French chemists was to add the phrases, with an excess of acid, or an excess of base, to the usual names. A method proposed by Dr Pearson is more concise and elegant. The genus being formed from the acid, when there is an excess of acid in a salt, the epithet *super* is prefixed to the name : when a deficiency of acid, the epithet *sub*. We thus speak of the Super-sulphate of Potash, the Subcarbonate of Potash, &c.

Where an acid is united with two bases, as is sometimes the case, the names of both bases enter into the name,— as the Sulphate of Alumina and Potash, or the Tartrate of Potash and Soda. Or sometimes the name of one of the bases is prefixed, as the soda-muriate of platina, or the ammoniaco-muriate of magnesia.

The advantages of this nomenclature are obvious. By the mere name of any salt, its nature is pointed out, the memory is aided, and a facility is afforded in naming so extensive a series of compounds. In several respects, however, I have remarked, it has been rendered imperfect or erroneous by the progress of discovery.

One is with regard to the distinction of the different acids according to the difference of oxygenation from the same base. This is not the sole difference between them. The sulphuric, nitric and phosphoric acids contain more oxygen than the sulphurous, nitrous and phosphorous; but besides this they contain hydrogen, or, according to the common doctrine, combined water ; and in a systematic nomenclature, this difference requires to be expressed.

This has been done by prefixing the epithet *hydro*, as hydro-sulphuric, hydro-nitric acid, &c. There is an objection to this, that it is rather the term to be applied to the acid formed by hydrogen with the radical; and Gay-Lussac has, on this principle, given the name of hydro-sulphuric acid to sulphuretted hydrogen, and of hydro-chloric, and hydro-cyanic to muriatic and prussic acids. Considering, however, the terms sulphuric, &c. as denoting an acid containing oxygen, the prefixed epithet hydro may be employed, without impropriety, to denote the addition of water, or of hydrogen. Or, perhaps, to avoid all ambiguity, that of ox-hydro or ox-idro might be employed.

Another deficiency is in denominating the acids which contain hydrogen alone. Gay-Lussac's method might be employed, but it is ambiguous, as denoting the presence of water rather than of hydrogen; and hydro-sulphuric, in particular, cannot be properly applied to sulphuretted hydrogen, both from this circumstance, and from its having been already applied to common sulphuric acid. Yet as the acidity of this compound is undoubted, its name, as well as the names of the compounds it forms with alkaline bases, ought to have some analogy to those of other acids and their salts. A systematic nomenclature would be to derive the name of an acid from its radical,—to prefix the syllable *oxy* when it is formed by oxygen, *hydro* when formed by hydrogen, and *oxidro* when formed by both. We should thus have the series of oxy-sulphuric, hydro-sulphuric, and oxidro-sulphuric acids, and the names of the salts formed by these might be derived from them. But this might be too great an innovation, and is objectionable, as being theoretical. The common terms may be retained with their usual signification; and the best mode probably of denominating those acids which contain hydrogen only, is to follow the principle of the nomenclature, retain the name of the radical in that of the acid, and express the distinction by a variation of termination. The

first syllable of the word hydrogen might be admitted into the name; we should thus have for sulphuretted hydrogen, for example, the name of sulphurid, sulphuridic, or sulphidic acid, and its salts might be named sulphurides or sulphides.

The names applied to the neutral salts, so far as they imply that the acid and base exist in their composition, are hypothetical, but understood merely as applied to compounds formed from these, may be employed, and are preferable to the introduction of new theoretical terms.

A variation has been introduced in the nomenclature, to denote the salts formed by different proportions of the acid with the base. The usual mode is not always admissible, as although the compound with the higher proportion of acid is a super-salt, that with the lower is not neutral; at least this is not the case in those with carbonic acid, and, in this respect, the terms carbonate and super-carbonate are incorrect. The higher proportions of acid being twice, thrice, or four times the quantity in the first, Dr Wollaston introduced, as applicable to those compounds, the prefixing the numerals denoting the series to the generic term, as carbonate and bi-carbonate of soda, oxalate and bin-oxolate of potash, quadroxalate, &c.

It is sufficient to have stated these general observations. Under individual cases, I shall employ that nomenclature which is most conformable to general usage.

The following Table by Kirwan gives the composition of the principal salts. Though it is not altogether correct, I insert it as being frequently referred to, as well as a smaller table by Berard of the composition of salts free from water. Dr Wollaston's scale gives the composition of those salts which it includes with more accuracy: under the individual salts will be found the composition assigned on the principal authorities.

No. 1.—Table of Kirwan.

SALTS.	BASE.	ACID.	WATER.	STATE.
Carbonate of potash	41.	43.	16.	Crystallized
Pearl-ash	60.	30.	6.	Dry
Carbonate of soda	21.58	14.42	64.	Fully crystallized
ditto	59.86	40.05	-	Desiccated
barytes	78.	22.	-	Natural or ignited
strontites	69.5	30.	-	Natural or ignited
lime	55.	45.	-	Natural if pure *
magnesia	25.	50.	25.	Crystallized
common ditto..	45.	34.	21.	Dried at 80°
Sulphate of potash	54.8	45.2	-	Dry
soda	18.48	23.52	58.	Fully crystallized
ditto	44.	56.	-	Desiccated at 700°
ammonia	14.24	54.66	31.1	
barytes	66.66	33.33	-	Natural and pure *
strontites	58.	42.	-	Natural and pure *
lime	32.	46.	22.	Dried at 66°
ditto	35.23	50.39	14.58	Dried at 170°
ditto	38.81	55.84	5.35	Ignited
ditto	41.	59.	-	Incandescent
magnesia	17.	29.35	53.65	Fully crystallized
ditto	36.68	63.32	-	Desiccated
Alum	12. †	17.66	51 ‡	Crystallized
Ditto	63.75	33.25	-	Desiccated at 700°
Nitrate of potash	51.8	44.	4.2 §	Dried at 70°
soda	40.58	53.21	6.21 §	Dried at 400°
ditto	42.54	57.55	-	Ignited
ammonia	23.	57.	20.	
barytes	57.	32.	11.	Crystallized
strontites	36.21	31.07	32.72	Crystallized
lime	32.	57.44	10.56	Well dried in the air
magnesia	22.	46.	22.	Crystallized
Muriate of potash	64.	36.	-	Dried at 80°
soda	53.	47. ‖	-	Dried at 80°
ammonia	25.	42.75	32.25	Sublimed
barytes	64.	20.	16.	Crystallized
ditto	76.2	23.8	-	Desiccated
strontites	40.	18.	42.	Crystallized
ditto	69.	31.	-	Desiccated
lime	50.	42.	8.	Red hot
magnesia	31.07	34.59	34.34	Sensibly dry

* Or artificial ignited. † Ignited.
‡ Of crystallization +19.24 in the base.
§ Of composition. ‖ Aqueous, 38.88 real.

NO. 2.—TABLE OF BERARD.

SALTS.	BASE.	ACID.
Muriate of potash	66.66	33.34
———— of soda	57.00	43.00
Sulphate of barytes	67.70	32.30
———— of potash	57.24	42.76
———— of soda	47.22	52.78
Nitrate of potash	48.64	51.36
Carbonate of potash	53.81	46.19
———— of soda	44.38	55.62
Subcarbonate of potash	70.21	29.97
————— of soda	62.53	37.47

NO. 3.—TABLE OF THE SOLUBILITY OF SALTS IN ALCOHOL.

A number of salts are soluble in alcohol, and this property is often applied, especially to the analysis of mineral waters. I insert a Table by Kirwan of their degrees of solubility in alkohol of different specific gravities, the quantities being those dissolved by 100 grains of the solvent; the temperature, Kirwan adds, was from 60° to 70°, the time allowed to effect the solution in general twenty-four hours, though in some cases from two to three days.

SALTS.	Spec. grav. 0.900	Spec. grav. 0.872.	Spec. grav. 0.848.	Spec. grav. 0.834.
	Grs.	Grs.	Grs.	Grs.
Sulphate of soda, ...	0.	0.	0.	0.
———— magnesia, ...	1.	1.	0.	0.
Nitrate of potash, ...	2.76	1.	0.	0.
———— soda, ...	10.5	6.		0.38
Muriate of potash, ...	4.62	1.66		0.38
———— soda, ...	5.8	3·67		0.5
———— ammonia, ...	6.5	4.75		1.5
———— magnesia, ...	21.25		23.75	36.25
———— barytes, ...	1.		0.29	0.185
———————- crystallized, ...	1.56		0.43	0.32
Acetate of lime, ...	2.4		4.12	4.75

TABLE OF THE SOLUBILITY OF SALTS IN WATER, BY KIRWAN.

THE following table shews the solubility of a number of salts in water. The quantities expressed are those dissolved by 100 parts of water at the temperatures of 60° and 212°.

SALTS.	Temperature.	
	at 60°.	at 212°.
Nitrate of potash,	14.3	100
———— soda,	33	100
———— ammonia,	50	200
———— barytes,	10	30
———— strontites,	100	200
———— lime,	200	
———— magnesia,	100	200
Sulphate of potash,	6	20
———— soda,	35	120
———— ammonia,	50	100
———— lime,	0.2	
———— magnesia,	60	130
———— copper,	25	50
———— iron,	16.5	
———— zinc,	33	
Super-sulphate of argil and potash, (alum),	6.5	50
Carbonate of potash,	25	80
———— soda,	50	100
———— ammonia,	30	100
———— magnesia,	2	
Subcarbonate of potash,	100	
Phosphate of potash,	very soluble.	
———— soda,	25	60
———— ammonia,	25	
———— magnesia,	2	
Muriate of potash,	33	50
———— soda,	40	41
———— ammonia,	33	100
———— barytes,	16.5	
———— strontites,	150	
———— lime,	200	
———— magnesia,	very soluble	
———— quicksilver,	5	50
Hyper-oxymuriate of potash,	6	40
Hyper-oxymuriate of soda,	33	100
Sub-borate of soda, (borax,)	8.3	16.6
Super-oxalate of potash,		16
Tartrate of potash,	40	
Super-tartrate of potash,	1.6	3.3
Tartrate of potash and soda,	20	
———————— antimony,	6.5	
Acetate of potash,	100	
———— soda,	33	
———— lead,	3	

CHAP. I.

OF NITRIC ACID, AND THE COMBINATIONS OF ITS BASE WITH OXYGEN.

This acid is one of those which has been longest known to chemists. The salt named Nitre consists of it combined with potash ; and the method of procuring it from this salt, in a diluted state, was known to the alchemists. The base of the acid is Nitrogen ; and this principle having been already considered as a constituent of atmospheric air, we have only to deliver under this chapter the history of the acid, and of the other compounds which are form-ed by the union of its base with oxygen in different pro-portions.

NITRIC ACID is the compound of nitrogen with the lar-gest proportion of oxygen. With smaller proportions are formed two gaseous compounds, both destitute of any acidity, one named formerly Nitrous Gas, to which the more appropriate appellation of NITRIC OXIDE is given ; the other denominated NITROUS OXIDE. There is an in-termediate compound between these and Nitric Acid, what is named Nitrous Acid, which some have regarded as of definite composition, while others have considered it as nitric acid, with an addition of nitric oxide in variable quantities. The two oxides conform to the general law of definite proportions, the quantity of oxygen in the one being twice the quantity in the other,—nitrous oxide be-ing composed of two volumes of nitrogen and 1 volume of oxygen, or by weight of 100 of the former with 57.14

of the latter, and nitric oxide of equal volumes, or by weight of 100 of nitrogen with 114,28 of oxygen. But in the other compounds, the regular progression is not traced, and there are considerable difficulties in assigning the proportions, and completing the series. Nitric acid, too, is the ternary compound containing hydrogen, or, according to the common doctrine, containing combined water, from which it cannot be freed in its insulated form. For convenience of arrangement, it may first be considered.

SECT. I.—*Of Nitric Acid.*

NITRIC acid has been long known in a state more or less pure: the corrosive acid liquor known by the name of Aquafortis is an impure and weak nitric acid ; and chemists had been acquainted even with the acid in a pure form, before they had any knowledge of its composition. Priestley observed the production of nitric oxide gas from it in various processes, and the reproduction of the acid when that gas was again mixed with oxygen, and Lavoisier drew the obvious conclusion, that the acid is a compound of these two gases *. But the nature of nitric oxide gas itself was then unknown ; and it is to Cavendish that we are indebted for a knowledge of the composition of nitric acid.

The experiment by which it was demonstrated, consisted in taking the electric spark for a considerable time in atmospheric air confined in a narrow glass tube over quicksilver. Priestley had observed, that in an experiment of

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* Mémoires de l'Acad. des Sciences, 1776, p. 671.

this kind the air is diminished in volume, and an acid is generated, infusion of litmus introduced being changed to a red; but the nature of this acid was not ascertained. Cavendish had supposed that it might be carbonic acid, but by making the experiment over a solution of potash, which served to neutralize the acid, he found that it was nitric acid; its smell was obvious, and paper dipt in the solution burnt with deflagration, as it would have done from being dipt in a solution of nitrate of potash. He farther found the generation of acid to be promoted by the addition of oxygen gas to the atmospheric air. When five parts of the former and three of the latter were exposed to the action of the electric spark, the mixture almost wholly disappeared. The same result was obtained from a mixture of oxygen and nitrogen gases in the proportion of seven of the former to three of the latter by measure; with less oxygen than this, there remained a portion of uncombined nitrogen. In this experiment, the nitrogen gas is, by the agency of the electric spark, brought into combination with the oxygen, and the nitric acid is the resulting compound [*]. The combination presents the phenomena somewhat singular, that it takes place very slowly, requiring the constant agency of the electric spark, and that no emission of light, nor sensible production of heat, attends it.

The combination of these gases, and the formation of nitric acid, was afterwards effected by presenting them to each other in a different state. Mr Milner found, that in passing the vapour of ammonia through an ignited glass or earthen tube containing black oxide of manganese, nitric oxide is formed, which, by a further oxygenation, gives nitric acid, the oxygen of the oxide combining in its nas-

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[*] Philosophical Transactions, vol. lxxv, p. 572; vol. lxxviii. p. 261.

cent state with the nitrogen of the ammonia *. Bayen obtained even nitric acid from the decomposition of black oxide of manganese by heat alone, probably from the combination of the disengaged oxygen in its nascent state with a small portion of nitrogen, the existence of which has been observed in this metallic oxide †.

The composition of nitric acid is likewise established by its analysis. If it be transmitted through an earthen or glass tube at a red heat, it is converted into oxygen and nitrogen gases: It suffers a similar decomposition from heat, when combined with an alkaline base: Or, if the acid be acted on by an inflammable substance or a metal, part of its oxygen is abstracted, it is converted into nitric oxide, which by a farther abstraction of oxygen is reduced to nitrogen; and even in some cases, where the attraction of the substance to oxygen is strong, the decomposition of the acid is complete, and nitrogen gas is evolved.

It has been found difficult to determine with accuracy the proportions in which the elements of nitric acid are combined, and in particular to reconcile them with those of the other nitrous compounds conformable to the usual laws of definite proportions. From the different experiments of Cavendish, the proportions were not uniform, as the production of the acid being influenced by circumstances, it was not uniformly the same. Taking the experiment which appears most accurate, they would be fixed at 72.2 of oxygen, and 27.8 of nitrogen. Lavoisier found the proportion of oxygen higher, that of 80 to 20. But his experiments were liable to fallacies, of which he was not sufficiently aware. Davy endeavoured to determine the proportions, in an indirect mode;—by the analysis of nitric oxide, then adding to it oxygen gas, forming a standard

* Philosophical Transactions, vol. lxxix, p. 300.
† Opuscules Chimiques, tom. ii, p. 180.

nitrous acid, the composition of which was thus known, and discovering what quantity of nitric acid this nitrous acid contained. He stated them at 70.5 oxygen, 29.5 nitrogen *. Converting these last proportions into those by volume, they give 100 of nitrogen with 208 of oxygen gas. Now, from the law that gases combine in simple proportions estimated by volume, and considering also that this law is observed in the two first compounds, nitrous oxide being composed of 100 volumes of nitrogen, and 50 volumes of oxygen, and nitric oxide of 100 volumes with 100, it must appear not improbable, as was suggested by Gay-Lussac, that the composition in nitric acid will be 100 of nitrogen with 200 of oxygen by volume, the slight deviation from this arising from errors of experiment. He accordingly found, that on adding to 200 measures of nitric oxide gas over water, 200 of oxygen gas, there is an absorption of 300, and 100 of oxygen remain, proving that 200 measures of the former combined with 100 of the latter, forming what he inferred to be nitric acid; and this, from the known composition of nitric oxide, gives as the composition 100 measures of nitrogen with 200 of oxygen †. Converting these into weight, they afford the proportions of 30.5 of nitrogen, and 69.5 of oxygen, or 100 of the former with 228 of the latter. Now, nitrous oxide being composed of 100 of nitrogen with 57 of oxygen, and nitric oxide of 100 with 114, these give the proportions of oxygen in the simple multiples of 1, 2, 4 in the three compounds.

The intermediate compound, nitrous acid, might be expected to supply the intermediate multiple 3. Gay-Lussac found, that on adding nitric oxide gas in excess (400 measures) to 100 measures of oxygen, there is an absorp-

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* Researches, p. 38.
† Mémoires d'Arcueil, t. ii, p. 216. 237.

tion of 400, and a residue of 100 of nitric oxide, shewing
that 300 had combined with 100 of oxygen. The pro-
duct he considered as nitrous acid. These proportions
are equivalent to 150 of nitrogen by volume to 250 of
oxygen; and converting them into weight, they amount to
34.5, to 65.5, or 100 of nitrogen with 190 of oxygen.
But this is too large a proportion to correspond with the
regular progression, which would require to be 100 of ni-
trogen with 171 of oxygen.

It has farther appeared, that the estimate of the compo-
sition of nitric acid of 100 of nitrogen and 228 of oxy-
gen, which gives the multiple 4 of the latter, cannot be
maintained. From its equivalent weight, as inferred from
its salts, Dr Wollaston states the proportions at 26 of
nitrogen with 74 of oxygen, or 100 with 285 *. Sir H.
Davy inferred from experiment, that 2 volumes of nitric
oxide gas combine with 1.5 of oxygen gas as a maximum
to form nitric acid, equivalent to 100 of nitrogen with
250 of oxygen by volume, and by weight 100 with 277,
or in 100 parts 26.5 with 73.5 †. And Berzelius assigns
the same proportions from experiment ‡. Now, this com-
position of nitric acid gives 5, as the multiple of oxygen
compared with the first proportion of that element, and
thus the whole series, with the exception of the two first
compounds, nitrous and nitric oxides, is irregular.

More lately Gay-Lussac, relinquishing his former view,
has proposed another, as removing these difficulties. He
assumes the existence of two acids, intermediate between
nitric oxide and nitric acid; one, which he names per-ni-
trous acid, formed by the condensation of 100 of oxygen and
400 of nitrous gas, and obtained also from the decomposi-

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* Philosophical Transactions, 1814, p. 11.
† Elements of Chemical Philosophy, p. 261.
‡ Annals of Philosophy, vol. ii, p. 283.

tion of nitrate of lead by heat, composed of 100 volumes of
nitrogen with 150 of oxygen ; and another, nitrous acid
vapour, formed by the condensation of 100 of oxygen and
200 of nitrous gas, and composed of 100 of nitrogen with
200 of oxygen by volume.   These give the multiples 3
and 4 of oxygen to the first proportion in nitrous oxide ;
and as he admits also the composition of nitric acid to be
that of 100 of nitrogen with 250 of oxygen, we have the
series in the whole compounds of 1, 2, 3, 4, and 5 of oxy-
gen by volume to 1 of nitrogen *.

Mr Dalton, who had formerly represented the series of
compounds in five proportions, by the assumption of an
oxy-nitric acid, composed of 19.5 of nitrogen with 80.5 of
oxygen, has more lately given a view similar to Gay-
Lussac's, only with a different proportion of oxygen. This
through the whole is stated about $\frac{1}{4}$th higher, the propor-
tion in nitrous oxide being 100 of nitrogen with 62 of
oxygen by volume, instead of 100 with 50, and the same
proportion of 62 being added in each successive combi-
nation.   But this cannot be reconciled with the experi-
ments of others.   The proportions, in particular, of the
two first compounds of 100 with 50, and 100 with 100,
seem to be sufficiently established ; yet without those (de-
viating from these) which Mr Dalton assigns, his nitric
acid formed of 1 measure of oxygen with 1.2 measures of
nitric oxide gas cannot be brought to correspond to his
proportion of 100 of nitrogen with 310 of oxygen for that
acid, nor otherwise is there any proof that any such acid
exists †.

But farther, Dulong has lately investigated the compo-
sition of Gay-Lussac's per-nitrous acid, obtained from the
decomposition of nitrate of lead by heat, and has found

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* Annales de Chimie et Physique, tom. i, p. 404.
† Annals of Philosophy, vol. ix, p. 186.

that it does not differ essentially from his nitrous acid. It contains, he found, no water; and the proportion of nitrogen to oxygen in its composition is 100 to 233.8 by weight, very nearly the same as that assigned by Gay-Lussac to nitrous acid vapour, which is 100 to 228 by weight. Dulong farther found, that the nitrous acid vapour, formed in the method employed by Gay-Lussac of mixing nitric oxide and oxygen gases without admitting water, is capable of being condensed, by reduction of temperature, into a liquid having all the properties of the acid obtained from the decomposition of nitrate of lead. There can be no doubt, therefore, that the two acids are the same *. The whole difficulty therefore recurs ;—we have in the two oxides, and in nitrous and nitric acids, the progression of the proportion of oxygen in the irregular series of 1, 2, 4 and 5 to 1.

Nitric acid of the composition of 100 of nitrogen with 285 of oxygen by weight is hypothetical : no such binary compound can be obtained insulated : these proportions represent only these elements as they are supposed to exist in binary combination in a nitrate, supposing also the base of the nitrate to remain an oxide. And nitric acid in its usual state always contains, according to the common expression of the fact, a portion of combined water, that is, is a ternary compound of nitrogen, oxygen and hydrogen. This is proved by its yielding a considerable proportion of water, when it is combined, in the highest state of concentration in which it can be procured, with a base : and that it cannot exist insulated without this water or its elements is shewn by the circumstance, that nitric oxide gas and oxygen gas combine easily over water in such proportions as to form nitric acid : but without the presence of water these proportions cannot be established ; they combine

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* Annales de Chimie et Physique, tom. ii, p. 317.

only with a lower proportion of oxygen so as to form ni-
trous acid,—and by the fact, that nitric acid, as a binary
compound, cannot be expelled from those compounds in
which it is supposed to exist ; it is either decomposed, or
water must be supplied to preserve its constitution.

The quantity of combined water has been variously es-
timated ; but it appears to be fixed, with sufficient preci-
sion, at 25.1 in 100 parts, at the specific gravity of 1.50 ;
and at this it is marked in Dr Wollaston's scale. And
considering this water as existing in the state of its ele-
ments, and nitric acid as a ternary compound of nitrogen,
oxygen and hydrogen, this gives as the composition 19.4
of nitrogen, 77.7 of oxygen, and 2.9 of hydrogen.

Still this view of the constitution of the acid does not
contribute to solve the preceding difficulty ; for the pro-
portion of oxygen to the nitrogen is that of 400 to 100,
and this gives 7 as the multiple of oxygen compared with
that in the first compound, which is just as discordant as
that of 5, from the regular progression.

It may be questioned, however, whether this be the real
quantity of water essential to the constitution of the acid :
and sufficient evidence may be given that it is not. The
acid to which this proportion is assigned is that of the
usual specific gravity 1.50. But this is not the highest
state of density in which nitric acid can be obtained. It
is procured with certainty at 1.55 at 60°, and it has been
affirmed at 1.58, or even 1.60. It evidently, therefore, at
1.50 contains water as an adventitious ingredient. In the
usual process by which it is obtained, that of decomposing
nitrate of potash by sulphuric acid, such a quantity of the
latter acid is necessary, as is afterwards to be stated, as to
afford two equivalents of combined water. Now one of these
only may be considered as entering into the constitution of
the nitric acid ; the other is not essential to it, though it is
capable of being only partially abstracted. Admitting

this view, which is farther confirmed from the relation of the elements in the dry nitrates, and admitting the theory of the constitution of the acid which I have illustrated, the acid of the specific gravity 1.50 is composed of 87.5 of acid and 12.5 of water ; and 100 of nitric acid are composed of 22.3 of nitrogen, 76 of oxygen and 1.7 of hydrogen *. This gives a proportion of oxygen which affords the multiple 6, to the first proportion in nitrous oxide.

The series, then, according to this view, in the nitrous compounds, is that of 1, 2, 4, 6 of oxygen to 1 of nitrogen, 100 of nitrogen being combined in nitrous oxide with 57 of oxygen, in nitric oxide with 114, in nitrous acid with 228, and in nitric acid with 342. This is a progression sufficiently regular. The proportions of 3 and 5 may perhaps exist, that of 3 in an acid intermediate between the nitrous acid and nitric oxide, and that of 5 in the composition of the salts named Nitrites, though this, as will afterwards appear, is far from being established.

Nitric acid is always procured from the nitre of commerce, a salt in which the acid exists in combination with potash. The process consists in adding to nitre a substance which, exerting an attraction to the potash sufficiently strong to weaken that of the nitric acid, allows it to be expelled by the application of heat. For this purpose, clay, sand, sulphate of iron, and some other substances, have been used ; but they require the assistance of a considerable heat, which causes a loss of acid by decomposition. The process introduced by Glauber is now

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* An acid of this strength, there is reason to believe, would have a specific gravity of about 1.62. And an acid of this specific gravity is said to have been procured by Proust.

therefore always followed, in which the nitrate of potash is decomposed by sulphuric acid. Four parts by weight of the salt, in coarse powder, are to be put into a glass retort, and three parts of sulphuric acid are poured upon it by a retort funnel. The retort is placed in a sand bath, and connected with a range of two or three globular receivers, in the last of which a small quantity of water is put, and which is not accurately closed. Heat is applied, and continued as long as any acid drops from the neck of the retort, being raised towards the end nearly to redness. The whole of the acid nearly condenses in the first receiver, a small portion is condensed in the second, and the water the third contains absorbs more effectually any nitrous acid vapour. Towards the end of the process, when the temperature is high, a quantity of permanently elastic fluid is disengaged, which is pure oxygen, and which may be collected by connecting with the last receiver a bent tube, which is made to terminate in the pneumatic trough.

In this process the sulphuric acid combines with the potash of the nitre, and disengages the nitric acid, so that by the application of the heat it is volatilized. It was known to practical chemists, that to obtain the full product of nitric acid, it is necessary to add more sulphuric acid than is necessary to saturate the quantity of the potash contained in the nitre ; and unless this larger quantity be employed, a considerable portion of the nitric acid is either not expelled, or, if the heat is raised very high, is lost by decomposition. Dr Wollaston has remarked, that as much sulphuric acid ought to be employed as is necessary to form with the potash of the nitre, bi-sulphate of potash ; and the proportions above stated, which are rather more of sulphuric acid than it has been usual to employ, are conformable to this view. The affinities exerted in this case may be supposed to be that of the sulphuric acid to the po-

tash, forming sulphate of potash, and that of the sulphate
to the additional portion of acid to form the bi-sulphate;
these may be more powerful than the first attraction alone,
and hence may facilitate the disengagement of the nitric
acid with less heat.   At the same time the additional por-
tion of water supplied by the larger quantity of the sul-
phuric acid will contribute to preserve the composition of
the nitric acid.   The acid, however, from this circum-
stance, receives, as was remarked by Dr Wollaston, two
equivalents of water from the sulphuric acid, one equiva-
lent more, as I have already illustrated, than is strictly ne-
cessary in the state of its elements to its constitution.

The acid, however, is never obtained without a partial
decomposition; for, although it is nitric acid which exists
in the salt, it is nitrous acid that condenses in the recei-
ver.   When the heat is first applied, vapours are disen-
gaged of a yellow tinge; in a short time they become co-
lourless, and continue so for part of the distillation, appa-
rently from the water in the materials being volatilized, and
preventing the decomposition; but towards the end of the
process, when this is exhausted, and the temperature is
raised high, a partial decomposition of the acid takes place;
a portion of its oxygen separates and assumes the elastic
form; a quantity of nitric oxide is thus produced, which,
communicated to the nitric acid, renders it coloured and
fuming, or converts it into nitrous.

A farther process, therefore, is necessary to convert the
product into nitric acid.   It is put into a glass retort con-
nected with a large receiver containing a little water. Heat
is applied by a water-bath, the nitric oxide is disengaged,
taking with it a portion of acid, and forming nitrous acid
vapour, which condenses in the receiver.   As this pro-
ceeds, the acid in the retort loses its colour, and at length
becomes colourless.   It is then the proper Nitric Acid.
Another method is to distil the nitrous acid from a little

black oxide of manganese, which, communicating to it oxygen, converts it into nitric.

As the nitre of commerce has generally a small portion of muriate of soda adhering to it, it yields a little muriatic acid, and sometimes a minute portion of sulphuric acid passes over. When nitric acid is to be employed for more delicate chemical purposes, it is necessary that these should be separated, which may be done by dropping into the acid a solution of nitrate of silver as long as it occasions any precipitation. The precipitate is allowed to subside, and the acid, to render it perfectly pure, is subjected to a second distillation.

Nitric acid is a colourless transparent fluid, having a peculiar odour, and emitting white vapours when exposed to the atmosphere. It possesses, in an eminent degree, the general acid properties ; it is highly corrosive, and erodes or burns vegetable and animal matter, tinging it first of a yellow colour ; even when largely diluted with water, its taste is extremely sour, and it instantly reddens the vegetable colours. Its specific gravity, as obtained by the preceding process, is about 1.5. Mr Dalton remarks, that by previously fusing the nitre, and using a strong sulphuric acid, it may be obtained of the specific gravity of 1.52. By distilling it with a gentle heat, it is brought, according to Kirwan's statement, to 1.55 ; and it has been stated even, according to Proust, at 1.62.

It has been an object of much investigation to determine the proportion of acid in diluted acids of different specific gravities ; but the results have been rendered uncertain, by being involved with the question of what constitutes real acid, and of referring to this as the standard. And accordingly the tables that have been given are so discordant, and involved so much in hypothesis, as to be entitled to little consideration. According to the common doctrine, which supposes real nitric acid to be the binary compound of oxygen and nitrogen, combined with a

base in a dry nitrate, acid of the specific gravity of 1.50 contains, as has been already remarked, according to Dr Wollaston's estimate, 25.1 of combined water in 100. If the view I have stated be just, it contains only half this quantity; the other portion existing in the state of its elements in the composition of the acid. The proportion, however, assigned by Dr Wollaston, represents the acid such as it is supposed to exist in the dry nitrates according to the common opinion, and the quantity of this in the acid of the specific gravity of 1.50. The real acid free from adventitious water, there is reason to believe, from the law of the condensation in the different proportions with water, would be of the specific gravity of about 1.62.

Nitric acid, in its highest state of concentration, is congealed by cold, but the part which freezes is not of the same strength as that which remains unfrozen. Cavendish remarked, that there is a degree of strength at which it freezes with less cold than when it is either stronger or weaker, but the strength of the acids he employed not being estimated by their specific gravities, scarcely any precise account can be given of the results. The congelation which took place with the least degree of cold was that where the acid was of such a strength as to dissolve $\frac{418}{1000}$ of its weight of marble, the freezing point of this acid being —2°. When the acid was either stronger or weaker, it required to freeze it a greater degree of cold, and the part frozen approached nearer that strength than the portion which did not freeze. When of the strength which Mr Cavendish denotes by $\frac{561}{1000}$, it required to be cooled to —41.6; and when so weak as to be at $\frac{276}{1000}$, it did not freeze till cooled to —40.3 [*].

Nitric acid is volatilized by heat; its boiling point varies, according to its concentration. According to Dalton, the acid of the specific gravity of 1.42 boils at 248°;

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[*] Philosophical Transactions, vol. lxxviii, p. 173.

this is the highest boiling point of the liquid acid in any state; and if it be either stronger or weaker than this, it boils at a lower temperature : as it becomes weaker, its boiling point approaches nearer to that of water, but cannot fall below this : the boiling temperatures of the stronger acids are lower, and become so progressively; that of the specific gravity 1.52 boils at about 180 or 185. The acid of the specific gravity 1.42 is also, according to Mr Dalton, the only one which rises unchanged in boiling; if an acid of inferior strength be distilled, the portion which first distils over is weaker, while in an acid of greater strength, what first distils over is stronger; the continued boiling, therefore, of nitric acid of any strength, brings it nearer to the strength of 1.42, and to the boiling point of this 248° *.

Nitric acid is decomposed by heat. It suffers a partial decomposition at a temperature of 212°, acquiring a yellowish tinge. When exposed to ignition, by passing it through a red-hot earthen tube, it is resolved into oxygen and nitrogen gases. It is partially decomposed by light : exposed to the solar rays, it acquires a yellow tinge from the formation of nitrous acid, and oxygen gas is evolved : if exposed sufficiently long, it becomes of a deep yellow.

Nitric acid has an attraction to water; it attracts it from the atmosphere, and it combines with it with great facility in all proportions, the combination being attended with the production of heat from diminution of capacity. If poured on ice or snow, it dissolves it rapidly, with a production of cold from the sudden liquefaction of the snow or ice. According to Cavendish's observations on the congelation of the acid, this cold is greatest either when the acid is of considerable strength, or when it is considerably diluted, while there is an intermediate strength where the cold produced cannot exceed —2, as at that point the

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* Chemical Philosophy, p. 348.

liquid formed by the acid with the snow freezes at that
temperature; the cold produced must for the same reason
be regulated by the proportions. By adding four parts of
nitric acid of the full strength to seven parts of snow, the
temperature falls to —30.

This acid is not affected by any of the simple gases at
a moderate temperature. At the temperature of ignition,
hydrogen decomposes it by combining with its oxygen. At
low temperatures it is partially decomposed by almost all
inflammable substances, which attract a greater or less pro-
portion of its oxygen: thus charcoal decomposes it with
rapidity, and if the charcoal be very dry, and the acid high-
ly concentrated, combustion is even produced. Some sub-
stances which contain carbon, as the essential oils, are al-
so inflamed by it; it likewise communicates oxygen to sul-
phur and phosphorus. The metals, too, decompose it, at-
tracting its oxygen more or less completely, and thus evol-
ving nitric oxide, nitrous oxide, or nitrogen gas: The me-
tallic oxides formed from these actions generally remain
combined with a portion of it undecomposed, and form
soluble compounds; and hence nitric acid is the most ge-
neral solvent of the metals.

Nitric acid combines with the alkalis, earths, and me-
tallic oxides; its salts are named Nitrates. In power of
saturation it is inferior to several of the other acids; hence,
if this power is to be regarded as a measure of the force
of attraction it exerts, that attraction must be less strong;
from the state of condensation, however, in which it exists
without any accompanying cohesion, it is capable of exert-
ing energetic actions; but its facility of decomposition li-
mits its action, and this, with the tendency of its elements
to pass into the elastic state, either pure or combined, ren-
der its compounds easily decomposed.

The generic characters of the Nitrates, at least of those
with alkaline or earthy bases, are a cool penetrating taste,
affording oxygen gas at a high temperature, deflagrating

at the temperature of ignition with inflammable bodies, and
affording white or yellowish vapours with concentrated sul-
phuric acid. They are all crystallizable. The composi-
tion of these salts is not easily determined by analysis, as
there is no re-agent by which nitric acid is precipitated.
It is therefore usually inferred from synthetic experiments;
the quantity of salt formed by the combination of a given
weight of nitric acid with the respective bases being as-
certained. The individual nitrates will be considered un-
der their respective bases.

Sect. II.—*Of Nitrous Acid.*

It has been stated, that in the process of decomposing
nitre by sulphuric acid with heat, the acid which distils
over is of a yellow colour. This coloured acid has been
even longer known to chemists than the colourless; it was
denominated Nitrous Acid, a name retained in the new
nomenclature.

In conformity to the theory, which regards acidifiable
bases as capable of existing in two definite states of oxyge-
nation, forming two distinct acids, nitric and nitrous acids
were considered as standing in this relation; the former
being a compound of nitrogen with a larger, the other with
a smaller proportion of oxygen. Another opinion, how-
ever, was also proposed. It was known that nitric acid, on
receiving nitric oxide gas, acquires the yellow colour and
fuming property of nitrous acid. If, through the liquid ni-
tric acid, a stream of nitric oxide gas be passed, the acid
first acquires a pale straw colour; then the yellow becomes
more predominant; it gradually deepens, as the gas is trans-
mitted to the orange; becomes at length nearly red; it as-
sumes, by a farther addition, successively, an olive green,

a bright green, and a bluish green; and, finally, if the addition of nitric oxide be continued, becomes so saturated with it as to pass into the elastic state, forming a dense, red-coloured vapour. Now, in all these stages of the experiment there is no indication of any fixed or uniform combination; and hence it was held, that there is no nitrous acid, or compound of oxygen and nitrogen in determinate proportions, different from those which constitute nitric acid, but that what is called such is merely nitric acid holding in solution variable quantities of nitric oxide. This seemed to be farther confirmed, by its being found, that by applying heat to the coloured acids, nitric oxide gas, holding a portion of acid in combination, is volatilized, and nitric acid remains.

There was one fact observed by Scheele, which favoured the opinion of the existence of a specific acid, to which the name of Nitrous might be applied. When a nitrate, or salt containing nitric acid, nitrate of potash, for example, is exposed to a low red heat, oxygen gas is expelled; and if the heat is not continued too long, a salt remains, which, when submitted to the action of an acid, yields vapours of nitrous acid. The nitric acid in this experiment losing oxygen, was supposed to be converted into an acid at a lower degree of oxygenation, which remained in union with the alkaline base. But the result is ambiguous. Nitric oxide may exist in the combination condensed by its affinity to nitric acid, and may furnish, when the salt is decomposed by another acid, a product of nitrous acid, conformable to the opposite opinion; and it has never been clearly shewn that any acid of uniform composition can be obtained insulated by this experiment.

There is another mode in which it has been supposed that an acid of specific constitution may be formed. Nitric oxide gas and oxygen gas combine with great facility when presented to each other, and form a dense red coloured acid vapour. The proportions in which the ga-

ses combine are much influenced by circumstances, parti-
cularly by the presence of water; the more freely water is
admitted, the proportion of nitric oxide to oxygen con-
densed being larger.   Now, it has been supposed, that
there must be a maximum quantity, which may be attained
by presenting the gases with an excess of nitric oxide ; it
is also conceivable, that in this combination, the oxygen
added may unite with the nitric oxide in such a manner
as to raise directly the degree of oxygenation of the nitro-
gen, and thus form a compound of the two ultimate ele-
ments of definite composition.   On this principle, Gay-
Lussac inferred the existence of such a compound.   In
mixing nitric oxide gas and oxygen gas over water, in the
proportion of 400 measures of the former and 100 mea-
sures of the latter, the absorption, he found, amounts to
400, and 100 measures of nitric oxide remain ; 300 mea-
sures of it, therefore, have combined with 100 of oxygen,
and this is the largest quantity which he could condense.
Nitric oxide consists of equal volumes of nitrogen and oxy-
gen ; this result, therefore, gives the proportion of 150 of
nitrogen to 250 of oxygen, or 3 to 5, by volume; and con-
verting these into weight, it gives as the composition of
nitrous acid, supposing this compound to constitute it, 100
of nitrogen with 190 of oxygen, or in 100 parts, 34.5 of
the former, and 65.5 of the latter [*].

The whole of this investigation, however, is doubtful or
incorrect. As the agency of water is admitted, and is in-
deed necessary to cause so large a proportion of the nitric
oxide to combine with the oxygen, there can be no certain-
ty but that it may influence the proportions, causing by its
affinity to the nitric oxide, or nitric acid, a larger or small-
er quantity of the former to enter into combination than
what constitutes nitrous acid, supposing such a compound
to exist. It appears too, from Mr Dalton's experiments,

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[*] Mémoires d'Arcueil, tom. ii, p. 238.

that when water is very freely admitted, even a larger quantity of nitric oxide gas, that of 3.6 to 1 of oxygen, may be combined. And what perhaps affords a conclusive objection to the opinion that this is a definite compound, is, that the proportions do not correspond, (as has been already stated, p. 199.) with the law of multiples, as applied to the other nitrous compounds.

When 400 measures of nitric oxide gas with 100 measures of oxygen gas are mixed together over a strong solution of potash, Gay-Lussac has subsequently affirmed [*], that by this arrangement the whole can be condensed, and an acid is formed which combines with the potash, and from these proportions must be composed of 100 of nitrogen with 150 of oxygen by volume. This he has named Per-nitrous acid, though the epithet Subnitrous would have been more appropriate; it cannot be obtained insulated, but only in combination with a base, or a small proportion of water. When nitric oxide gas and oxygen gas are presented to each other in exhausted vessels, they combine and form a dense red coloured vapour, and the degree of condensation which attends the combination, when different proportions are mixed, is that which results from the union of 100 volumes of oxygen gas with 200 volumes of nitric oxide gas, and is equal to this latter volume. This product Gay-Lussac considers, therefore, as another acid of specific composition, capable of remaining insulated in the gaseous state, but decomposed by water, or by the action of an alkaline base. He gives it the name of Nitrous acid, or Nitrous acid vapour; and from these proportions it must be composed of 100 of nitrogen with 200 of oxygen. Lastly, when nitrate of lead is decomposed by heat, a yellow coloured acid, apparently of uniform appearance and properties, is obtained, which had been examined by

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[*] Annales de Chimie et Physique, t. 1, p. 394.

Berzelius[*], and regarded by him as the proper Nitrous acid. According to Gay-Lussac, it is the same with the Per-nitrous. And the proportions in these two acids, the per-nitrous and nitrous, are such, it has already been remarked, as to afford the multiples 3.4 of oxygen to 1 and 2 in the two oxides, — a proof, therefore, it may be inferred, of their existing as definite compounds.

Dulong, however, it has been already noticed, has established other results[†]. Submitting to analysis the acid procured from nitrate of lead by heat, he found it to contain no combined water, contrary to what Gay-Lussac had supposed; and on calculating the proportion of nitrogen to oxygen in its composition, he found it to be composed of 100 of the former to 233.8 of the latter by weight: now these differ altogether from those of Gay-Lussac's per-nitrous acid, while they differ little from those of his nitrous acid, which are 100 to 228. It followed from this, that the latter, existing in the state of vapour at its formation, must be capable of being condensed into the liquid form ; and, accordingly, Dulong found, that on transmitting dry nitric oxide gas and oxygen gases, in the proportion of rather less than twice the volume of the former to one volume of the latter, into a curved tube, cooled to 20 below zero, (4° below 0 of Fahr.) he obtained a greenish liquid, which emitted yellow vapours, and which, during decantation, passed into a yellow coloured fluid, having all the properties of the acid procured from the decomposition of nitrate of lead. This left, therefore, no doubt of the identity of the two. Its not having been obtained liquid before in its production from the combination of the two gases, is owing to its not having been submitted to a low temperature, and to an excess of one or other of the gases being generally pre-

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[*] Annals of Philosophy, vol. ii, p. 276.

[†] Annales de Chimie et Physique, t. ii, p. 317, translated in Philosophical Magazine, vol. xlviii, p. 331.

sent, which contributes to retain it in the elastic form ; and
the larger the proportion of foreign gas is, the more diffi-
cult is its condensation.

Is this acid then to be regarded as one of specific com-
position, the proper Nitrous acid ? The circumstances, that
it can thus be obtained insulated by the combination of the
two gases in a determinate proportion ; that it is capable
of being condensed in the liquid form ; and that it is uni-
form in composition, as formed by two processes so differ-
ent as that of the direct action of nitric oxide and oxygen,
and the decomposition of nitrate of lead, favour this con-
clusion ; and it is perhaps sufficiently established by the
fact, that its composition is conformable to the law of de-
finite combinations, its proportion of oxygen being a sim-
ple multiple, as has already been remarked, of that in the
lower nitrous compounds.

This acid affords an example of a binary acid.   Dulong
proved that it contains no water.   When decomposed at
a red heat by the action of a metal abstracting its oxygen,
the elastic product he found to be nitrogen, without any
intermixture of hydrogen.   It is formed, too, from dry
nitric oxide and oxygen gases, without the admission of
water ; and in the other process which affords it, the de-
composition of nitrate of lead, no water is present, that
salt containing none.   Its production from this salt ap-
pears to depend on the weak affinity of the nitric acid to
oxide of lead, so that the acid admits of being decomposed
at a moderate heat ; it is thus resolved into nitrous acid
and oxygen gas ; if a higher heat were necessary, the ni-
trous acid would itself suffer decomposition, and hence the
products of the decomposition of other nitrates by heat are
chiefly nitrogen and oxygen gases.

This acid, Anhydrous nitrous acid, as Dulong named it,
has a specific gravity, he found, of 1.451 ; it is of a deep
orange colour, but this is at a natural temperature ; its co-
lour becomes deeper as it approaches its point of ebulli-

tion, and is at length nearly red ; if cooled below 60, it
becomes paler, at 32° it is of a fawn colour, at 14° it is
nearly colourless, and at 4° it is entirely so. It emits va-
pours copiously, and boils at 82.5 of Fahrenheit.

It is decomposed by water. When mixed with a large
proportion of water, there is an immediate disengagement
of nitric oxide gas ; if a small quantity of water has been
added, there is no evolution of gas, but the acid becomes
of a very deep green colour ; and hence, if the acid be al-
lowed to drop into water, it becomes green as it reaches
the bottom : this appears to be owing to the decomposi-
tion of a part of the acid into nitric acid, while the remain-
der receives the nitric oxide, for the orange acid itself ac-
quires a green colour by being impregnated with nitric
oxide gas.

It is absorbed by sulphuric acid without decomposition,
and forms a solid crystalline substance. When it is pla-
ced in contact with a strong solution of potash, Dulong
found that it is decomposed, nitric oxide gas is disenga-
ged, though in smaller quantity than when the same de-
composition is produced by water ; nitrite and nitrate of
potash are formed. With liquid ammonia the action is
extremely violent, and the nitric oxide gas extricated is
mixed with nitrogen gas, proving that part of the ammo-
nia has been decomposed. When it is passed in vapour
over dry barytes in a tube at the common temperature, the
vapour is slowly absorbed ; but at a temperature of above
400°, the barytes becomes incandescent ; no elastic fluid
is extricated ; the compound melts, and is afterwards very
difficult to dissolve ; it affords nitrate and nitrite of barytes.
From these results, it appears that nitrous acid cannot be
brought into direct combination with the salifiable bases,
since either nitric oxide is disengaged, or nitric acid is
formed, proving a partial decomposition. This had been
before remarked even with regard to the common colour-
ed acids considered as nitrous, and hence it remained un-

certain, if the salts named Nitrites could be obtained pure.
An indirect method was employed for their formation, that
pointed out by Scheele with regard to common nitre, of
exposing it to such a heat as to expel a portion of the oxy-
gen of the acid.   On pouring on the residual salt any
weak acid, such as vinegar, acid fumes of a red colour are
disengaged.   But it is uncertain whether the proper ni-
trous acid exists in these compounds, or whether merely a
portion of nitric oxide is retained in combination with part
of the nitric acid attached to the base.   Berthollet found,
that the salt formed in this way from nitre is alkaline *, a
circumstance which would rather lead to the latter opi-
nion ; and the properties at least of the pure nitrites may
be considered as unknown.   The salts commonly named
Nitrites have generic characters similar to the nitrates,
with the peculiar distinctive property of giving vapours of
nitrous acid, when submitted to the action of another acid:
they are also said to absorb oxygen from exposure to the
air, and to return to the state of nitrates.

Nitrous acid acts on inflammable bodies, and on me-
tals, as nitric acid does, and even in its common state has
been said to impart oxygen more readily ; it thus kindles
pyrophorus, and phosphorus inflames in its vapour.

It still remains to be determined what is the nature of
the acid named by Gay-Lussac Per-nitrous, formed from
the condensation of 4 volumes of nitric oxide with 1 vo-
lume of oxygen over a solution of potash.   It is evident,
if it be a definite compound, that it contains much less
oxygen than nitrous acid, and from the proportions it fol-
lows, as has been already remarked, that it affords the inter-
mediate multiple of oxygen between nitrous acid and ni-
tric oxide.   But as it cannot be obtained insulated, little
certain can be said with regard to it ; it may be merely
nitrous, or nitric acid, retaining an excess of nitric oxide

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* Mémoires de l'Acad. des Sciences, 1781, p. 30.

in combination with the base, or the water with which it is combined. Mr Dalton has stated, too, that he has been unable to obtain the results with regard to the combination of the two gases described by Gay-Lussac *. Dulong found, that on employing Gay-Lussac's proportions, 4 volumes of nitric oxide and 1 of oxygen, and exposing the mixture to a low temperature in a tube, a liquid condensed; but it was of a deep green colour, and much more volatile than the nitrous acid. On submitting it to analysis, it afforded, in one experiment, 207 of oxygen to 100 of nitrogen; in another 216,—proportions of oxygen less than that of nitrous acid, but greater than that of the per-nitrous acid. It might therefore either be a compound or mixture of nitrous acid with another acid containing a smaller proportion of oxygen, or a simple solution of nitric oxide in nitrous acid; there is no conclusive evidence for either opinion. When it was exposed to heat, the green colour became weaker, and at length the yellow nitrous acid remained. It has already been remarked, that when this anhydrous acid is added to water, by which it is decomposed, and nitric oxide evolved; if the quantity of water is not too large, a green colour is acquired, which must be ascribed, as Dulong remarks, to a part of the nitrous acid being converted into nitric, and to the remainder retaining the nitric oxide; and this favours the opinion, that the green acid formed in the above experiment is nitrous acid, surcharged with nitric oxide.

When nitric acid absorbs directly nitric oxide gas, it passes through numerous shades of colour, first yellow, then orange, then olive, and green. Sir H. Davy gave the following short table of the proportions of these different coloured acids.

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* Annals of Philosophy, vol. x, p. 83.

Pale yellow, Real acid, 90.5. nitric oxide 1.2. water 8.3.
Bright yell. ——— 88.94. ————— 2.96. ——— 8.10.
Dark orange ——— 86.84. ——— — 5.56. ——— 7.6.
Light olive ——— 86.0. ————— 6.45. ——— 7.55.
Dark olive ——— 85.4. ————— 7.1. —— 7.5.
Bright green ——— 84.8. ————— 7.76. ——— 7.44.
Blue green ——— 84.6. ————— 8.0. ——— 7.4.*

The changes of colour are likewise dependent on the
degree of dilution. If the dark orange-coloured acid be
mixed with water, the different shades are produced, blue
appearing with a large quantity of water, with more acid,
olive, and bright green ; hence also, if nitric oxide be add-
ed to the nitric acid somewhat diluted, the yellow colour
is not produced but only the green.   These colours Gay-
Lussac supposes to arise from changes in the density of
the acid.   They are not permanent; the oxygen loosely
dissolved in the water, or imbibed from the atmosphere,
bringing the whole to the state of nitric acid.   Even the
concentrated coloured acids, when exposed to the atmo-
sphere, if they are secluded from light, absorb oxygen and
become pale.   The nitric acid, by these combinations with
nitric oxide, has its specific gravity diminished ; a pale
acid of 1.52, when converted into yellow acid, becoming
nearly of the specific gravity of 1.51.   It also becomes
more volatile : hence its fuming property ; and by impreg-
nation with the gas the acid at length assumes the elastic
form, constituting a dense red vapour.   Similar changes
are produced by the action of any substance abstracting
oxygen from the acid, such as the addition of a small quan-
tity of inflammable matter, or the chemical agency of light.
The different yellow coloured acids contain portions pro-
bably both of nitric and nitrous acid, the latter predomi-
nating as the colour deepens to orange or red.

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* Researches, p. 37.

As the chemical properties of the acid in these states do
not differ materially from those of nitric acid, the acid
procured from the decomposition of nitre by heat, which
has always a yellow colour more or less deep, is in com-
mon use, under the name of Nitrous acid, for many of the
purposes to which nitric acid, were it equally economical-
ly obtained, would be applied.   The acid also is general-
ly used diluted, and in this dilution it soon passes to the
state of nitric, or in the combinations into which it enters
any nitric oxide present is disengaged ; while in other
cases it is formed, and its presence therefore is unimpor-
tant.   It is extensively employed in several arts, particu-
larly for etching on copper, and in some of the processes
of dyeing, as well as in the art of assaying.   It is an agent
of the first importance in chemistry, from the facility with
which it parts with oxygen, and dissolves the metals.   It
is used in medicine as a tonic.   Under the form of vapour,
it has been successfully employed to destroy contagion.
The *aquafortis* of commerce is nitric acid diluted, and ge-
nerally impure from the admixture of muriatic and sul-
phuric acids.   Double *aquafortis* is about half the strength
of the common nitrous acid, and single *aquafortis* half the
strength of the other.

SECT. III.—*Of Nitric Oxide.*

THIS compound of nitrogen in a lower degree of oxy-
genation than nitric acid, exists when uncombined in the
gaseous form.   It was first observed by Hales, who took
notice of one of its most striking characters, the conversion
of it into a red vapour, when mixed with atmospheric air.
Priestley is the proper discoverer of it : he observed its
production in the solution of different metals in nitric acid,

obtained it insulated, and examined its chemical proper-
ties.   He gave it the name of Nitrous Air ; for which that
of Nitrous Gas was substituted.   This name is not suffi-
ciently appropriate, as there are other nitrous compounds,
(nitrous oxide, or nitrous acid vapour,) to which it may be
equally applied   It has therefore been named Nitric Oxide,
this distinguishing it from nitrous oxide, and the final syl-
lable *ic* denoting a higher degree of oxygenation, the cir-
cumstance which constitutes the difference between them.
The name is not perhaps strictly proper, since this sylla-
ble is in the new nomenclature appropriated to the names
of acids ; but it is preferable to the vague term Nitrous
Gas.   It may be named also Deutoxide of Nitrogen.

Nitric oxide is not formed by the combination of oxy-
gen and nitrogen gases; for, when presented to each other,
under the circumstances which cause their intimate com-
bination, they unite in those proportions which form ni-
tric acid.   It is procured, therefore, by decomposing the
acid by the action of substances, which partially abstract
its oxygen.   In some of these decompositions, the action
is not always limited, so that the oxygen shall be abstract-
ed in that proportion which converts the acid into nitric
oxide : it frequently proceeds farther, and portions of ni-
trous oxide and of nitrogen are evolved.   Hence some
substances are better adapted than others to evolve pure
nitric oxide.

Of the metals this character belongs to quicksilver and
copper.   The latter may in general be preferred, as the
decomposition of the acid goes on with more regularity,
and the process is more easily conducted.   One part of
small copper-wire, or of copper-filings, is put into a re-
tort ; one part of nitric acid, of the usual strength, diluted
with 4 or 5 of water, is poured upon it, and a very mode-
rate heat is applied by a taper ; or, what has been prefer-
red by other chemists, the nitrous acid is diluted with on-
ly an equal part of water, and no heat applied; in either

case, the decomposition of the acid takes place; the copper abstracts a portion of its oxygen, and converts it into nitric oxide gas, which is disengaged, and, by placing the extremity of the neck of the retort beneath an inverted jar filled with water, may be collected. The oxide of copper remains in combination with a portion of the acid. The nitric oxide, from the action of copper on nitric acid of the specific gravity 1 26, according to Davy, seldom contains more than from $\frac{1}{30}$ to $\frac{1}{50}$ of nitrogen, when it has been received through common water: when boiled water has been used, the quantity is not more than $\frac{1}{210}$. That from mercury and nitric acid is nearly of the same purity *.

This production of nitric oxide in these processes sufficiently indicates its composition. The acid imparts oxygen to the metal, and a portion of it combines with the metallic oxide: of course the nitric oxide, which is the other product of the process, is to be regarded as a compound of oxygen and nitrogen, containing less oxygen than the acid.

There are some indirect modes in which nitric oxide is formed, from which its composition may be inferred. Dr Milner found, that in passing ammoniacal gas over black oxide of manganese raised to a red heat, nitrous gas is produced; it derives its origin from the oxygen of the oxide of manganese uniting with the nitrogen of the ammonia, while the hydrogen of the ammonia unites with another portion of oxygen and forms water †.

The composition of nitric oxide is also established by its analysis. By the action of the electric spark, it is converted into nitrogen and nitrous acid. It had often been stated not to be decomposed by heat directly applied,—a result rather singular, since it is decomposed by electricity; but Gay-Lussac found, that on passing it through a

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* Researches, p. 194.

† Philosophical Transactions, vol. lxxix, p. 300.

tube of devitrified glass with platina wire included at a red heat, it is converted into nitrogen and nitrous acid; the platina suffers no change, but is used merely to favour the decomposition, by imparting heat to the gas *.

The analysis of nitric oxide is best effected by the action of such substances as have a strong attraction to oxygen. Thus, if it be exposed to a mixture of iron-filings and sulphur moistened with water, or to humid sulphuret of potash, or if charcoal, pyrophorus, phosphorus, or iron be heated in it, it is converted either into nitrous oxide, by the partial abstraction of its oxygen, or in some of the experiments, particularly in the latter, the decomposition is complete, and nitrogen gas is the residuum. Davy found, that on heating charcoal in a measured quantity of the gas, by the aid of a lens, the nitric oxide was converted into nitrogen; and from the quantities of carbonic acid and nitrogen gas produced, he inferred that it consists of 56.5 oxygen, and 43.5 nitrogen by weight : or, correcting this estimate by mean calculations derived from the decomposition by pyrophorus, and by hydrogen, 55.95 oxygen and 44.05 nitrogen †. Converting the proportion by weight into that by volume, it gives, Gay-Lussac remarked, as the relative quantities of the two gases, 50 of nitrogen and 54.45 of oxygen. In conformity to the law, he observed, of elastic fluids combining in simple proportions by volume, he supposed this deviation, from the proportion of equal volumes, to have arisen from errors of experiment; and he accordingly found, that on burning potassium in 100 measures of nitric oxide gas, exactly 50 measures of nitrogen gas remained ‡. This was confirmed by Davy. And as some doubts had been maintained with regard to it, Gay-Lussac has more lately

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* Annales de Chimie et Physique, tom. i, p. 398.

† Researches, p. 139.

‡ Mémoires d'Arcueil, tom. ii, p. 216.

confirmed it by new experiments. On heating 100 volumes of it with sulphuret of barytes, he obtained in one experiment a residue of nitrogen of 50.2, in a second of 49.5, and in a third in which tin was employed 48.8. The mean is 49.5; and that the real result is 50 can scarcely be doubted *. Nitric oxide, therefore, consists of equal volumes of oxygen and nitrogen; and by weight of 53.24 of oxygen, and 46.76 of nitrogen. The combination appears to be without any condensation, the density of the gas being exactly that of the two gases.

Nitric oxide is permanently elastic. It is colourless, and therefore from its rarity invisible. Its specific gravity to that of atmospheric air is, according to Berard, 1.0388, by calculation it must be 1.0370.

Nitric oxide gas proves extremely deleterious to animal life. Warm-blooded animals die almost immediately on a full inspiration of it, and the irritability of the heart is completely destroyed. Insects which live in other noxious gases are quickly killed by immersion in it, and fishes die in water impregnated with it. It proves even noxious to vegetable life, the leaves of a growing plant soon becoming withered in it, and the plant dying.

Nitric oxide gas exposed to distilled water is absorbed to the amount, according to Priestley, of about one-tenth of the volume of the water. Davy found that 100 cubic inches of water, previously boiled strongly with the exclusion of atmospheric air, absorbed 11.8 cubic inches of nitric oxide gas. According to Dalton, water free from air absorbs about $\frac{1}{18}$th of its bulk of nitric oxide gas. The water does not acquire any taste or any sensible acidity, unless it hold oxygen loosely dissolved. Both Priestley and Davy found that the gas is expelled from the water unchanged at a temperature of 212°. With spring water, the absorption appears to be less; which may be partly

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* Annales de Chimie et Physique, tom. i, p. 399.

owing to the air in the water being expelled.   Less is absorbed by hard water, that is water holding earthy salts in solution, than by water which has no such saline impregnation.

The impregnation of water with certain metallic salts enables it to absorb much larger quantities of nitric oxide gas, and this absorption presents results with regard to which different opinions have been formed.   Priestley observed, that a solution of green sulphate of iron in water absorbs 10 times its volume of nitrous gas, acquiring at the same time a deep olive colour, and at length becoming black [*].   As in the green sulphate the metal is at a minimum of oxidation, and as it is known to have an attraction to more oxygen, so as to absorb it from the atmosphere, it seemed probable that in this absorption the gas is decomposed, its oxygen being attracted by the salt, — a supposition which appeared to be confirmed by a fact observed by Priestley, that a similar change of colour is produced in the metallic solution by the addition of a few drops of nitric acid; and by another not less favourable to it, that there is no great absorption of nitric oxide by the solution of the sulphate, in which the metal is, at the maximum of oxidation.   Nitrogen too was found in the residual air, another proof apparently of this decomposition.

Vauquelin and Humboldt supposed the changes to be even more complicated than these. The solution of sulphate of iron impregnated with nitric oxide, they found reddened the tincture of turnsole; when sulphuric acid was added to it, it gave vapours of nitric acid; and, when saturated with potash, exhaled ammonia.   They concluded, therefore, that a portion of water is likewise decomposed, the oxygen of which, combining with the nitric oxide, forms nitric acid, while its hydrogen unites with a portion of the nitrogen of the oxide to form ammonia [†].   Davy,

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[*] Experiments on Air, vol. ii, p. 8.

[†] Annales de Chimie, tom. xxviii, p. 123, 181.

on the contrary, inferred, that the nitric oxide is not de-
composed, but merely absorbed.   If care be taken to avoid
the action of the atmospheric air, no sensible acidity can
be detected in the liquor ; and the gas may be recovered
unchanged, by removing the atmospheric pressure, while,
at the same time, the solution recovers its colour ; or if a
moderate heat be applied, the gas is expelled pure, and
the fluid loses its dark colour ; but from the alteration of
affinities by the temperature, a small quantity of ammonia
is formed, which precipitates a little oxide of iron.   The
residuum of nitrogen is, according to Davy, merely that
which is mixed with the nitric oxide ; and hence is deri-
ved an easy method of determining the purity of nitric
oxide gas *.   Berthollet, however, has still supposed, that
in these combinations of nitric oxide gas, a partial decom-
position takes place, that part of the nitric oxide is con-
verted into nitric acid, and ammonia formed † : and it
does not appear to have been proved by Davy's experi-
ment, that the whole of the nitric oxide gas is again ob-
tained, on the removal of pressure by the air-pump.

Some other metallic solutions exert similar actions on
nitric oxide gas.   A solution of green muriate of iron ab-
sorbs it more rapidly, and to a greater extent ; and it is
absorbed with changes of colour, by nitrate of iron, sul-
phate of tin, and sulphate and muriate of zinc ‡.

Nitrous gas has no acid properties.   Its solution in wa-
ter, freed from air, does not taste sour, nor does it redden
the vegetable colours.   Neither does this happen from the
introduction of the gas itself, previously washed in water
to remove any nitric acid vapour.   The colour, however,
I have observed, is impaired.

Nitric oxide gas is capable of supporting combustion ;
but this only, in some substances, and at an elevated tem-

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* Researches, p. 152.   † Statics, vol. ii, p. 127.
‡ Researches, p. 190.

perature. A lighted taper immersed in it is extinguished, as is also sulphur introduced in a state of inflammation. Phosphorus may be fused or sublimed without burning in it; but if introduced in a state of active combustion, it burns with great splendour. Another inflammable substance, pyrophorus, burns in it even at a low temperature. Charcoal, suspended in it in a state of ignition, burns very feebly. A number of the metals heated in it abstract its oxygen.

The most important and characteristic property of this gas is the facility with which it combines with oxygen, while, at the same time, it does not exhibit in this combination the phenomena of combustion. If presented to oxygen gas, they instantly combine, and red-coloured nitrous acid vapour is produced, which, if the experiment be made over water, is absorbed; if water be excluded, it retains the elastic form, a degree of condensation attends the combination, but to what extent is not easily ascertained, as the presence of water in the gases influences the result, and the products are various, according to the proportions of the two gases. Davy has stated, that when two measures of nitric oxide gas, and one of oxygen gas free from moisture, combine in an exhausted globe, they become condensed to about one-half of their volume, and orange-coloured nitrous acid vapour is formed. Gay-Lussac, on the other hand, affirms that the condensation amounts to two-thirds, or is equal to that of the nitric oxide in the above proportions *.

It is a striking circumstance attending this combination, that there is no sensible emission of light, and so little caloric is rendered sensible, that the vessel scarcely becomes sensibly warm.

The phenomena are similar when nitric oxide gas is presented to atmospheric air; the combination with the

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* Annales de Chimie et Physique, t. i, p. 402.

oxygen takes place with equal facility, red vapours are pro-
duced, which are quickly absorbed by water, and if the due
proportions are observed, the nitrogen of the air remains
pure.

Although the experiment appears simple, it has been
found difficult to determine with precision the proportions
in which this combination of nitric oxide with oxygen takes
place. Priestley, who first observed it with accuracy, found
100 measures of oxygen condensed entirely, or at least to
0.03, by 200 measures of nitrous gas, or 1 part by 2. By
others the greatest diversity of results have been stated.
The differences arise from the circumstance, that oxygen
and nitric oxide combine in different proportions, which
are determined by the circumstances under which the com-
bination takes place, so that, as Dalton has remarked, the
mixture may be so managed, that 10 measures of oxygen
shall take either 13 or 36, or any intermediate number of
measures of nitric oxide.

Thus, if we present the two gases to each other in an
exhausted glass globe, or over quicksilver, they combine,
and a red or orange vapour is formed, which remains per-
manent. From an experiment of this kind, the propor-
tions in which they combine to saturation cannot easily be
determined, since the nitrous acid vapour retaining the
elastic form, variable quantities either of oxygen or of ni-
tric oxide gas may remain combined with it ; and even if
condensed by cold, in the method of Dulong, already stated,
a portion remains elastic if there is any excess of either
gas, and the liquid is liable also to absorb a portion of the
nitric oxide.

The experiment, therefore, is performed over water, to
produce the condensation of the vapour ; but in doing so,
we introduce an agent which has an influence on the com-
bination, and the proportions become various according
as it is more or less freely admitted to the mixture. The
more largely the mixture of the gases is presented to wa-

ter, the less oxygen enters into combination with the nitric oxide, probably from the circumstance, that when a narrow surface of water is exposed, the absorption is slow, and the progress of the combination continues towards saturation, while, when the surface is large, the product from the first proportion of oxygen is absorbed as it is formed, and before the nitric oxide is saturated with oxygen. In the one case nitric acid, in the other nitrous acid, chiefly is formed.

According to Mr Dalton's experiments *, if 4 measures of oxygen gas are added to 1.3 of nitrous gas in a tube, two-tenths of an inch in diameter, and 10 inches long, 1 measure of oxygen combines with 1.3 of nitric oxide. But if 1 measure of oxygen, and 5 of nitric oxide gas, are mixed in a very wide vessel, so as to form a thin stratum of elastic fluid over the water, 1 of oxygen will take from 3 to 3½ of nitric oxide; and under other circumstances other results are obtained. Gay-Lussac stated the proportions somewhat differently. If the mixture of the gases is made in a narrow tube, with the proportion of 200 measures of nitric oxide, and 200 measures of oxygen, 200 of the nitric oxide combine with 100 of oxygen, and nitric acid is formed. But if 400 parts of nitric oxide gas are added to 100 of oxygen, the absorption is 400 parts, 300 of nitric oxide combining with 100 of oxygen, and nitrous acid is formed †. If the gases are mingled in different proportions, or placed under a different degree of exposure to water, the combination is established in intermediate proportions. The general principle is, that the presence of water favours the combination with the lowest proportion of oxygen, probably by absorbing the compound as quickly as it is formed : the exclusion of water has the opposite effect, allowing the nitric oxide to be saturated with oxy-

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* Chemical Philosophy, p. 327.
† Mémoires d'Arcueil, tom. ii, p. 235.

gen; and the limits seem to be that of 1 of oxygen with 1.35 of nitric oxide on the one hand, and that of 1 with 3.65 on the other. The mode of presenting the gases to each other also influences the result, which, as Mr Dalton has remarked, is owing to the circumstance, that when the nitric oxide gas is put into the tube first, and the oxygen added, the acid formed in the upper part, trickling down the sides, receives more oxygen in its progress; and hence, under this arrangement, nitric acid chiefly is formed. For a similar reason, the proportions of the gases have a considerable influence, an excess of oxygen favouring the production of nitric acid, and an excess of nitric oxide that of nitrous acid. Agitation, by favouring the absorption of the product, must likewise have an effect; and such is the operation of these circumstances, that it is difficult to establish perfect uniformity; two experiments, as Mr Dalton has remarked, performed apparently alike, giving different results *.

This property of nitrous gas, of combining with, and condensing oxygen gas, has been applied to the purpose of eudiometry. It constituted the first eudiometer: the only mode from which the purity of air was before judged of was by its effect on animal life; and Priestley, therefore, to whom this application of nitric oxide is due, justly considered it as a valuable acquisition.

The mode in which he employed it was extremely simple. One ounce measure was filled with the air designed to be submitted to trial, and this was introduced into a jar of $1\frac{1}{2}$ inch in diameter, inverted in water; the same measure of nitrous gas newly prepared was added to it; and the mixture was allowed to stand two minutes. If the diminution of volume were considerable, more nitrous air was added, till the oxygen in the air submitted to examination appeared to be saturated. The

* Memoir, Annals of Philosophy, vol. x, p. 38.

whole was then transferred into a glass tube two feet long, and one-third of an inch wide, graduated according to the air measure, and divided into tenths and hundredth parts. The space occupied by the residuum was thus measured, and compared with the quantity of airs mixed, so that the extent of diminution was ascertained; and as 1 measure of oxygen gas, according to Priestley, is condensed by 2 measures, or rather by 1.97 of nitric oxide gas, the quantity of diminution is divided by 3 or 2.97 to give the volume of oxygen. As much nitric oxide gas must always be employed as will saturate the quantity of oxygen in the air submitted to trial; and it is better to use even rather a slight excess, for certainty of effect, avoiding too much, as it may give rise to error by being absorbed. Thus, if atmospheric air is operated on, add 100 measures of it to 50 measures of nitric oxide gas in a jar of 1½ inch diameter, the whole will be reduced to 84 measures; the diminution therefore is 66, which divided by 3 gives 22 as the volume of oxygen.

Chemists found this method of ascertaining the quantity of oxygen difficult of execution, so as to be accurate, owing to the circumstances by which the results are influenced. Cavendish pointed these out at an early period [*], particularly the influence of agitation of the mixture, which renders the diminution greater, and of the order of mixing the gases, the diminution being greater, when the air is added to the nitric oxide gas, than in the reverse order. He also observed, that the nature of the water over which the experiment is made influences the result, the diminution being greater with distilled or rain water than with spring water; owing principally to the expulsion of the nitrogen loosely combined in water which has been exposed to the atmosphere, by the absorption of the nitrous acid, which adds to the bulk of the residuum.

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[*] Philosophical Transactions, vol. lxxiii, p. 106.

The purity of the nitric oxide gas, which some have thought essential, is not so, as though it may contain a little nitrogen this merely remains, and does not affect the condensation. If it contained nitrous oxide gas, this might give rise to some error by being absorbed.

The facility of this method is such, that notwithstanding these objections, some chemists are disposed to retain it; and it has one important advantage in common with hydrogen, that from the condensation being so great, any error of observation or measurement is much diminished. Mr Dalton has remarked, that in using it the experiment ought to be conducted in such a manner as to form either nitric acid or nitrous acid, and avoid the intermediate proportions, as these must be variable. This, as has been already explained, depends principally on the proportions in which the gases are mixed, and the more or less free admission of water. Of the two modes, that in which the influence of water is excluded, except in so far as to condense the product, in which case nitric acid is formed, is, according to Mr Dalton, most easily and most accurately effected. " In order to this, a narrow tube is necessary; one just wide enough to let air pass water, without requiring the tube to be agitated, is best. Let little more nitrous gas than is sufficient to form nitric acid be admitted to the oxygenous gas; let no agitation be used, and as soon as the diminution appears to be over for a moment, let the residuary gas be transferred to another tube, and it will remain without any further diminution of volume. Then $\frac{7}{9}$ths of the loss will be due to oxygen." In making the experiment, therefore, on atmospheric air, add 36 measures of nitric oxide gas to 100 of air ; avoid agitation ; ascertain the diminution of volume ; and multiplying this by $\frac{7}{9}$, the product gives the proportion of oxygen. The tube which Mr Dalton uses is represented Fig. 48.

Gay-Lussac has recommended the opposite mode, and

has affirmed, that in a narrow tube, and without a consi-
derable excess of nitric oxide, the results are variable. He
employs a very wide jar, and having placed in it 100 mea-
sures of atmospheric air, he adds 100 measures of nitric
oxide gas. A dense red vapour is immediately produced,
which disappears without agitation, and in a minute or
little more the absorption is complete. The residual gas
is transferred into a graduated tube, the degrees of which
correspond with the measures of the gases employed. The
absorption, according to Gay-Lussac, is uniformly about
84 parts, the fourth of this (according to his assumption
that 3 measures of oxygen combine with one of oxygen,
to form nitrous acid) gives the volume of oxygen, or 21
in 100 parts of atmospheric air. Judging from my own
experience, this latter mode has appeared to be prefera-
ble: and I have found, indeed, that the simple method
employed by Priestley, which is analogous to this, gives in
general a result sufficiently uniform. The combination of
nitric oxide with oxygen being so much influenced, how-
ever, by circumstances, the experiment may be liable to
give discordant results, in the hands of different experi-
mentalists.

Sir H. Davy proposed another method of applying nitric
oxide gas to eudiometry. He found that the solution of sul-
phate or muriate of iron, impregnated with nitric oxide,
absorbs rapidly the oxygen of atmospheric air. If a tube
graduated into 100 parts filled with atmospheric air be in-
troduced into a saturated solution of this kind, the absorp-
tion of the oxygen of the contained air, when favoured by
a slight agitation, will be completed in a few minutes; and
the diminution of volume will shew the quantity of oxy-
gen. It is necessary however to observe the progress of
the experiment carefully, as in a short time after the di-
minution is at a maximum, the volume of the residual gas
begins again to be enlarged, from the slow decomposition

of the nitrous acid formed during the experiment *. He
states the diminution obtained in this way at 21 in 100 :
but it is liable to uncertainty. An apparatus for employing
these solutions in eudiometrical experiments has been in-
vented by Mr Pepys, the liquid being put into an elastic
gum bottle, which is connected by a glass tube, when the
experiment is to be made, with a graduated tube contain-
ing the air ; by pressing the bottle, the liquid is made to
act on the air with a degree of compression, which favours
the result †. The method is rather complicated. It af-
fords, however, a useful instrument for separating other
aëriform fluids from each other, and ascertaining their pu-
rity, especially when liquids have to be used for these pur-
poses at a high temperature.

Nitric oxide does not combine intimately with nitrogen
or hydrogen gas, at moderate temperatures. If even the
electric spark be transmitted through the mixture with hy-
drogen, no inflammation or perceptible diminution is pro-
duced ‡. Or if such a mixture is transmitted through
an ignited glass tube, it does not suffer decomposition §.

Nitric oxide is likewise incapable of entering into com-
bination with the alkalis or earths. When the electric
spark is taken in the mixture of it with ammoniacal gas, a
mutual decomposition takes place, the oxygen of the oxide
combining with the hydrogen of the ammonia, forming wa-
ter ; if there is an excess of nitric oxide, a little nitric acid
is formed ; or if the ammonia is in excess, a portion of hy-
drogen is evolved. Gay-Lussac states, that nitrous gas
and ammoniacal gas act on each other at a common tem-
perature ; in about a month the mixture of equal volumes

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* Journals of the Royal Institution, p. 45.
† Philosophical Transactions for 1807.
‡ Davy's Researches, p. 136.
§ Berthollet's Chemical Statics, vol. ii, p. 122.

is reduced nearly to one half, and much nitrogen with nitrous oxide remains. He found, too, that nitric oxide exposed to a strong solution of potash was converted in about three months into nitrous oxide, and crystals apparently of a nitrite were formed *.

Sect. IV.—*Of Nitrous Oxide.*

This compound is not obtained by the combination of its constituent parts, but from the decomposition of nitric oxide or nitric acid, by substances which abstract oxygen. It was discovered by Priestley, who gave it the name of Dephlogisticated Nitrous Air. By the associated Dutch Chemists Messrs Deiman and Trootzwick, who also examined it, it was named Gaseous Oxide of Azote. Davy first obtained it in a state of purity, and discovered some of its most singular properties. He gave it the more concise appellation of Nitrous Oxide. It has since been named Protoxide of Azote, or of Nitrogen.

Priestley procured this gas by exposing nitric oxide to iron-filings moistened with water ; the nascent hydrogen disengaged from the decomposition of the water by the iron attracting part of the oxygen of the nitric oxide, and reducing it to the lower degree of oxygenation, which constitutes nitrous oxide. He found it also to be produced on placing nitric oxide in contact with a humid mixture of iron-filings and sulphur, or with the liquid compounds of sulphur with the alkalis. Kirwan obtained it by exposing nitric oxide gas to sulphuretted hydrogen, and the Dutch chemists by subjecting this gas to the action of muriate of tin, of copper dissolved in ammonia, and by pass-

* Annales de Chimie et Physique, t. i, p. 397.

ing it over heated sulphur *. In all these cases the change
of the nitric into nitrous oxide is owing to the partial ab-
straction of the oxygen of the former, by the substances to
which it is exposed.

Nitrous oxide is produced too during the solution of
several metals in nitric acid. Priestley observed its disen-
gagement during the solutions of tin, zinc, and iron, mix-
ed with variable quantities of nitric oxide gas and nitro-
gen gas ; its production being probably owing to the de-
composition of the water of the acid by the metal, the
nascent hydrogen of which, presented to the nitric oxide
which arises from the decomposition of part of the acid at
the same time, partially abstracts its oxygen, and brings it
to the state of nitrous oxide. Hence those metals which,
when dissolved in a diluted acid, do not decompose wa-
ter, as mercury, lead, bismuth, and antimony, give out on-
ly nitric oxide, with portions of nitrogen ; while nitrous
oxide is produced, during the solution of iron or zinc in
mixed sulphuric and nitric, or muriatic and nitric acids.

As obtained by all these processes, however, it is mixed
with variable quantities of nitrogen and nitric oxide gases,
from which it is not easily separated. It is disengaged
more pure in the decomposition of nitrate of ammonia, by
heat. The production of it in this case had been obser-
ved by Berthollet, but the circumstances relating to it
were determined with more accuracy by Mr Davy.

The nitrate of ammonia is obtained by evaporation of
its solution, either in prismatic crystals, or in a compact
mass. These varieties of it are decomposed at different
temperatures, the compact at a heat between 340° and
480° ; the fibrous at a temperature not lower than 400°,
but between that and 500°. In both cases water and ni-
trous oxide are the sole products. At higher temperatures
other affinities are exerted. At 600° the decomposition

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* Journal de Physique, tom. xliii, p. 324.

becomes rapid, a luminous appearance is produced in the retort, and the gases evolved are nitric oxide, nitrous oxide, and nitrogen, mixed in variable quantities. When the temperature is raised to 700° or 800°, an explosion happens, and the products are water, nitrous acid, nitric oxide, and nitrogen gas *.

To procure nitrous oxide gas, then, nitrate of ammonia, either compact or fibrous, (the latter, according to Mr Davy, being preferable, as sustaining less loss by sublimation, before its decomposition commences,) is put into a tubulated glass retort, and is quickly raised to the requisite temperature, taking care not to exceed 500°, and, in particular, not to raise it so high as to produce any luminous appearance in the retort; this regulation of temperature is easily obtained by the heat of an Argand's lamp. The nitrous oxide with watery vapour are disengaged; the gas is received over water, as it is not immediately absorbed; it is generally turbid, from a small portion of the nitrate of ammonia being volatilized; but this is soon absorbed by the water over which it is received; and when it is prepared for the purpose of respiration, it should be allowed to remain an hour in contact with water, to deposite this, as well as a small quantity of acid which is suspended in it. Care should be taken that the nitrate is free from any intermixture of muriate, as this causes a formation of oxymuriatic acid. From 100 grains of compact nitrate of ammonia, about 85 cubic inches of nitrous oxide gas are obtained. One pound gives 4.25 cubic feet; while one pound of the fibrous salt gives nearly 5 cubic feet †.

The theory of the production of this gas by this process presents a striking example of a nice adjustment of affinities and of equivalent quantities. Nitric acid is a compound of oxygen and nitrogen; ammonia, a compound of hydrogen and nitrogen; the solid salt, therefore, con-

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* Davy's Researches, p. 112.   † Ibid. p. 121.

sists of oxygen, nitrogen and hydrogen, the affinities of which, at a moderate temperature, are balanced so as to form the binary combinations which constitute the acid and alkali. But when the temperature is elevated, the disposition of these elements to assume the elastic form subverts these affinities, and others are exerted, combining them in different modes and proportions ; the hydrogen of the ammonia combines with a portion of the oxygen of the acid, and forms water ; and the remaining oxygen of the acid combining with the nitrogen of the acid, and the nitrogen of the ammonia, forms nitrous oxide. The proof that this is the case, is, that none of the elements are evolved during the decomposition : nitrous oxide and water are the only products, and the elements of the salt must therefore have been combined in this manner for their formation. At a higher temperature, other forces are exerted. At ignition the nitrous oxide is decomposed, being converted into nitrous acid vapour, and a gas analogous to atmospheric air, composed of oxygen and nitrogen, loosely combined. Hence, when the temperature of the nitrate of ammonia is raised near to ignition, nitrous oxide can either not be formed, or, if it were, is immediately decomposed, and resolved into these or similar products.

From experiments on the formation of this gas, in the process now described, Davy inferred, that it is composed of 62.4 of nitrogen, with 37.6 of oxygen. This was confirmed by analysis. When the gas is detonated with hydrogen gas, rather more hydrogen than nitrous oxide being employed, the products are water and nitrogen gas ; the quantity of hydrogen consumed gives the proportion of oxygen derived from the nitrous oxide, and the remaining nitrogen indicates the proportion of it in the nitrous oxide. From this analysis, he fixed the proportions at 63.5 nitrogen, and 36.5 oxygen [*] : From its analysis by charcoal, at

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[*] Researches, p. 291.

a high temperature, the products being carbonic acid and nitrogen, he stated them in one experiment at 63 or 64 nitrogen, and 37 or 36 of oxygen : Taking the mean of the most accurate experiments, they may be said to be 63.3 nitrogen, and 36.7 oxygen *. With this the estimation of its composition by the Dutch Chemists agrees surprisingly, as they were not aware of some circumstances by which it is influenced ; the proportions they give are 62.5 nitrogen, and 37.5 oxygen †. Reducing the proportions by weight of 63.3 and 36.7 assigned by Davy, to the proportions by volume, the latter are 100 of nitrogen and 49.5 of oxygen ; an approximation so nigh to that of 2 to 1, as to be conformable to the law of Gay-Lussac, that elastic fluids combine in simple proportions regulated by the volume; and this chemist has found, that from the analysis of nitrous oxide by the combustion of potassium, 100 parts of it consist of 100 in volume of nitrogen and 50 of oxygen gas ‡.

Nitrous oxide is permanently elastic. Its specific gravity is, according to Davy, 1.614, according to Colin 1.5209 ; 100 cubic inches, according to the former estimate, weigh 50.1 grains. Its taste is distinctly sweetish, which is felt when it is respired. Its odour is very faint.

This gas is absorbed by water, the atmospheric air of the water being expelled by it ; at a mean temperature, and atmospheric pressure, 100 cubic inches of water absorb, according to Davy, 54 ; on boiling the solution, the gas is given out unchanged; the solution has a sweetish taste, and a slight odour, not disagreeable ; neither it nor the gas changes the vegetable colours.

Nitrous oxide gas suffers no diminution of volume, nor any change of properties, when mixed with oxygen, nitro-

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* Researches, p. 325.
† Journal de Physique, tom. xliii, p. 331.
‡ Recherches Physico-Chimiques, tom. i, p. 166.

gen, or hydrogen gas. At ignition, it detonates with hydrogen gas. It is decomposed by transmitting the electric spark through it, or passing it through an ignited earthen tube, being converted into nitrous acid, and oxygen and nitrogen gases.

A property eminently belonging to it is that of supporting combustion. A lighted taper burns in it with an enlarged and bright flame, nearly as in oxygen gas ; phosphorus with a dazzling white light ; sulphur with a rose-coloured flame ; and iron-wire with corruscations. The inflammable bodies, however, require to be raised to a higher temperature, to burn in nitrous oxide gas, than they do to burn either in oxygen gas or in atmospheric air. If sulphur be burning with a pale blue flame, on introducing it into the gas, it is extinguished : it is only when the temperature has been previously raised, to cause it to burn with the blue and white light, that it continues to burn ; phosphorus, which burns in atmospheric air at 100°, does not burn in nitrous oxide gas but when the temperature is above 212° ; and charcoal, and the compound inflammables, require to be in a state of high ignition for this combustion. During these combustions, a portion of nitrous acid is almost always produced, along with the product of the oxygenation of the combustible body *.

The most singular property of this gas is displayed in its action on the animal system, when received by respiration. It had been supposed to be noxious to life. Priestley found, that an animal confined in it is soon killed ; and the Dutch chemists made similar experiments on birds with the same result, and concluded that it is highly deleterious, from a theory they had formed of its agency, that it is incapable of affording oxygen to any substance but hydrogen, and that, therefore, it is unfit for abstracting the carbon of the blood, the principal office performed by

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* Researches, p. 322.

the air in respiration *. Mr Davy first observed its singular powers, his attention having been directed to its action on the living system, in consequence of a vague hypothesis which had been advanced, that it is the principle of contagion. He found it to operate as the most powerful stimulant, producing a high state of excitement both of body and mind, accompanied with very peculiar sensations not strictly analogous to those produced by any other stimulant, and generally by a propensity to muscular exertion, and the power of exerting it with greater energy. Similar effects were experienced by other individuals, varying, however, in combination and intensity, as might be expected ; of these, different relations have been given in Mr Davy's publication. One who has not experienced the effect may be disposed to regard them as exaggerated ; but a single trial is generally sufficient to dissipate this doubt. On some individuals, the effects produced have been unpleasant and depressing ; sometimes convulsions and other nervous symptoms have been occasioned by it : others have experienced the peculiar effects on the intellectual functions, the exhilaration, the crowding of indistinct ideas, and the propensity to muscular exertion, without the sensation of pleasure which generally accompanies it ; and in some individuals it has had no sensible effect. In the same individual, too, they are very different, at different times. The violent operation of it generally ceases in five or six minutes after ceasing to respire it, though sometimes a degree of excitement continues for several hours. The quantity of the gas which requires to be respired to produce the full effect is from 4 to 9 or 10 quarts ; and it is more powerful when breathed pure, than when diluted with atmospheric air or hydrogen gas. It cannot be breathed pure for more than $4\frac{1}{4}$ or 5 minutes. The larger warm-blooded animals confined in it die generally in five or six

* Journal de Physique, tom. xliii, p. 329. 332.

minutes; the smaller in one or two minutes.   It previous-
ly produces in them, at least frequently, exciting effects;
they become convulsed, and soon insensible; and in some,
the insensibility is induced at first.   They live, however,
in general, twice as long as in hydrogen gas or under wa-
ter; the lungs are inflamed; the blood is of a purple-red
colour; and the muscles are inirritable.   Amphibious ani-
mals are affected in a similar manner, but live rather long-
er.   Fishes put into water impregnated with it are soon
affected, and die in fifteen or twenty minutes.   And wing-
ed insects soon become motionless in the gas, and are kill-
ed in no long time.

It is not the least of the singularities in the operation of
this agent, that the excitement it produces is not followed
by languor or debility.   No law with regard to the living
system seems more general and invariable, than that in-
creased action excited by any agent is followed by a pro-
portional degree of lassitude and debility.   Nitrous oxide
furnishes a striking exception to this.   Notwithstanding
the high exhilaration it produces, this is not followed by
any marked exhaustion, but is reduced to that state of the
system which existed at its commencement, leaving, even
for a time, alacrity and pleasant feelings.

Davy examined the changes which the gas suffered in
respiration, with the view of illustrating the nature of the
agency it exerts.   He found, that after it had been breath-
ed for some time, a great part of it is absorbed, and the
residual gas is chiefly nitrogen; and that when exposed
to blood, it is in part absorbed, and the residual air is in
this case also chiefly nitrogen,—changes probably owing
in part to an absorption of the nitrous oxide, and partly
to its decomposition, and the abstraction of its oxygen by
blood.   The actual consumption of the gas, so as to pro-
duce the full exciting effects, does not appear to exceed a
pint.

Nitrous oxide was inferred by Davy to be capable of

forming combinations with the alkalis. They are not esta-
blished when the gas is presented to the alkali, either in
the dry state, or dissolved in water, but only when in its
nascent state. The process he employed consisted in ex-
posing a portion of the salt formed of potash with the sul-
phurous acid, sulphite of potash, having a quantity of pure
potash intimately mixed with it, over mercury to nitric
oxide gas ; the sulphite of potash decomposes the gas by
partially attracting its oxygen, and converts it into nitrous
oxide, which, as it is formed, is attracted by the pure po-
tash present. The sulphate of potash, into which the
sulphite is converted, and the compound of nitrous oxide
with potash, are in a great measure separated by solution,
evaporation and crystallization, at a low temperature. The
new compound consists, as nearly as could be estimated,
of about 3 of alkali and 1 of nitrous oxide by weight. Its
taste is caustic, with a pungency different from either po-
tash or carbonate of potash. It renders vegetable blues
green, probably from the intermixture of alkali. Pulveri-
zed charcoal mingled with a few grains of it, and inflamed,
burns with slight scintillations ; projected on zinc in a
state of fusion, a slight inflammation is produced. When
sulphuric, muriatic or nitric acid is introduced to it under
mercury, it gave out nitrous oxide mingled with a little
carbonic acid ; and carbonic acid thrown into a solution
of it in water, disengages nitrous oxide gas ; a proof of the
weak force by which the nitrous oxide is retained in com-
bination with the alkali. A combination of nitrous oxide
with soda is effected by a similar process ; but the gas does
not appear to be absorbed so largely as by potash. Cast
on zinc in fusion, it burns with a white flame. Heated to
400° or 500°, it gives out nitrous oxide rapidly. By fol-
lowing the same process with ammonia, lime, and stron-
tites, no combination was obtained. These compounds
were denominated Nitroxides *.

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* Researches, p. 262.

Nitrous oxide gas is absorbed by inflammable liquids, and in greater quantity than by water. Alkohol at 52 degrees absorbs more than its bulk ; acquir s a sweet taste, but in its other physical properties is not altered. The gas is expelled at the temperature of ebullition, and likewise by the combination of the impregnated alkohol with water. The absorption by ether, and the results of it are similar. The essential oils absorb it in still larger quantity, as do also the fixed oils, and from both it is expelled unaltered by heat *.

CHAP. II.

OF SULPHURIC ACID, ITS BASE, AND THEIR COMBINATIONS.

It was known to the Alchemists, that from certain metallic salts, which either exist native or which can be formed from certain metallic ores, a strong acid may be extracted by distillation. These salts had been named Vitriols ; and this acid being of great density, and having from this somewhat of an oily appearance, had received the name of Oil of Vitriol. The more correct appellation of Vitriolic Acid was afterwards given to it. In the progress of chemical researches it was discovered, that there exists a peculiar relation between this acid and sulphur, and it was at length demonstrated that this inflammable substance is its base. It was therefore named Sulphuric Acid. It is the product of the full saturation of sulphur with oxygen. Another acid is formed, from a smaller proportion of

* Researches, p. 240.

oxygen combined with the base, which, in conformity to the principles of the modern nomenclature, is named Sulphurous Acid. Besides these, sulphur combines with hydrogen, forming likewise an acid compound, and in a different proportion another compound having no acidity. The chemical history of these combinations is to be given in this chapter, beginning with that of the base.

Sect. I.—*Of Sulphur.*

THOUGH in conformity to the principles of the arrangement I follow, I introduce sulphur as the base of sulphuric acid, it is not from this acid that it is procured. It exists abundantly in the mineral kingdom, both pure and in a combined state. Native sulphur occurs in different forms ; the greater part of it is a volcanic production ; it is also found imbedded in gypsum and limestone, and sometimes in smaller quantity, in veins which traverse primary rocks. The sulphur of commerce is generally of volcanic origin, and the greater part of what is imported into this country is the produce of Sicily and Italy. Sulphur also exists in large quantity combined with some metals, particularly iron, copper, and lead; and it is sometimes extracted in the working of these ores, being volatilized, and condensed in flues ; but it can scarcely be procured sufficiently pure.

It exists in other states of combination in mineral substances. It is also a constituent principle of organised matter. In the spontaneous decomposition of some kinds of vegetable matter, especially of the plants named cruciform, it is sometimes deposited. Deyeux found, that in extracting a fecula from the roots of the dock, a quantity of sulphur is mixed with it, which could be separated by sub-

limation ; and also, that it could be extracted from the root of the horse-radish *.   In animal substances it is still more common and abundant, as is shewn by its evolution in their putrefaction or decomposition by heat.

The sulphur of commerce not being perfectly pure, it is purified by sublimation in close vessels.   It then exists in the form of a light powder.   The substance named *Sulphur vivum* appears to be the residuum of this sublimation ; and Roll sulphur is the common sulphur, generally impure, melted, and run into cylindrical moulds.

Sulphur, when solid, is brittle, and breaks even from the heat of the hand when grasped for a short time, owing probably to its imperfect conducting power, whence the expansion is not equally propagated through the mass.   By friction, it becomes electrical.   When rubbed, its peculiar odour is more perceptible.   Though of a yellow colour in mass, yet, when precipitated from some of its combinations, as from its combination with liquid potash by an acid, it is nearly white.   This whiteness of precipitated sulphur has been supposed to be owing to its combination with a portion of water, a supposition that appears to be proved by the whiteness which is also acquired by sulphur when it is sublimed into a vessel filled with watery vapour, or when water is dropped on it melted.

Sulphur is fused by heat.   According to Bergman, this takes place at about 224 of Fahrenheit ; while in fusion it has a red colour.   By slow cooling, it may be crystallized. Its crystallization in needles may often be perceived in breaking a roll of sulphur, and it can be effected easily by the process given by Rouelle, that of melting sulphur, allowing it to cool until it becomes solid to the thickness of half the mass, then pouring out the remaining liquid sulphur : the cavity is lined with needle-like crystals.   When dissolved in alkohol, or in essential oils, it is deposited, on

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* Journal de Physique, 1781, p. 242.

long standing, in minute crystals, which approach in form
to some of the varieties of native sulphur.

A singular phenomenon is presented in the action of
heat upon sulphur. When in fusion, if the heat be conti-
nued, instead of remaining fluid, it suffers the opposite
change, becomes thick and viscid, and this thickness aug-
ments for a range of temperature of 200 degrees. This
phenomenon was examined with attention by Dr Irvine
junior *. He found, that while the liquefaction of sulphur
takes place at about 226° of Fahrenheit, the thickening
begins at 320°, and continues and increases to 530 or 550,
at which temperature copious fumes arise. It can be re-
peated any number of times upon the same mass of sul-
phur, and is regularly followed by the diminution of the
thickness on the removal of the high temperature. On
pouring this viscid matter into water, it remains for a while
soft and tough, and even when solid retains a degree of
tenacity. Impressions can be taken by applying it to a
mold ; these form what have been named Sulphur Casts.

This change had been ascribed to oxidation ; and the
viscid matter had been regarded as an oxide of sulphur.
Dr Irvine found, however, that the unrestrained or the
difficult access of the air had no effect on the result ; and
that it depended entirely on the agency of caloric, as is
evident from the liquidity being recovered by reducing the
temperature. This thickening of the sulphur, as the tem-
perature rises, he found, was not accompanied with con-
traction ; for, on cooling sulphur from the temperature of
400, it continued contracting until it reached 226, its
melting point, when, in congealing, it expanded.

Sulphur is volatilized by heat, at nearly the same tem-
perature as that at which it melts. It condenses again
unchanged ; or at least with only a slight acidity from the
action of the air of the vessel. At a temperature very lit-

* Chemical Essays, p. 475.

tle higher, that of 300 nearly, it combines with oxygen,
and presents the phenomena of combustion. It gives a
pale blue flame, a considerable quantity of heat is rendered
sensible, and vapours are disengaged extremely suffocating
and pungent.   At a higher temperature, as that of full ig-
nition, it burns with a white flame.   In oxygen gas, the
light it emits is white with a shade of blue.   It combines
with oxygen in two proportions.   The product of its com-
bustion is an acid, which exists in the aërial form, Sulphu-
rous Acid.   It exists in Sulphuric Acid with a larger pro-
portion of oxygen, and probably a portion of hydrogen.
The existence of an oxide of sulphur has also been suppo-
sed, principally from the consideration, that from the re-
lative proportions of oxygen to sulphur in the two com-
pounds, sulphurous and sulphuric acids, the law of multi-
ples in chemical combinations implies a lower degree of
oxidation than that which constitutes the first, as is after-
wards to be illustrated.   Mr Dalton, too, brought forward
some cases of chemical action in which it was supposed to
be established * ; but the facts are inconclusive or uncer-
tain, and no such compound can be obtained insulated.

Sulphur combines with hydrogen, forming in one pro-
portion an elastic compound ; in another, a compound
which appears to be capable of existing in the liquid state :
there is reason to believe even that these combinations
may be established in various proportions.   It unites with
phosphorus likewise in different proportions.   It com-
bines with the greater number of the metals, and forms
compounds, a number of which retain the metallic lustre
and opacity : these combinations are established by fusing
the sulphur with the metal, and are generally accompanied
with an evolution of heat and light.   With the alkaline
metalloids it combines easily, the combination being ac-

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* Chemical Philosophy, p. 385.

companied with intense ignition, and compounds are form-
ed which are inflammable.

Sulphur combines with the alkalis and alkaline earths :
these compounds are of a reddish brown or gray colour ;
they are soluble in water, but at the same time decom-
pose it, and hence cannot easily be submitted to chemical
examination. When in solution, they absorb oxygen.
Their properties are to be afterwards considered.

Sulphur, so far as can be demonstrated, is a simple sub-
stance. The younger Berthollet stated some experiments,
from which he inferred that it contains hydrogen ; small
portions of that element being obtained in the mutual ac-
tion of sulphur and charcoal at a red heat ; in combining
sulphur with metals by fusion ; and in transmitting the va-
pour of sulphur through an ignited glass tube [*]. Sir H.
Davy, too, found, that when potassium is combined with
sulphur by heating them together, sulphuretted hydrogen
is produced : and when sulphur is submitted to the ac-
tion of a galvanic battery of high power, the same gas is
evolved to the amount of five times the volume of the sul-
phur. He farther inferred, that oxygen exists in sulphur,
principally from the assumption,—that oxygen is an ele-
ment in the constitution of sulphuretted hydrogen ; a con-
clusion in support of which he also brought forward some
experimental results [†].

Subsequent researches, however, have not given any sup-
port to these conclusions. Gay-Lussac and Thenard point-
ed out the sources of fallacy which gave rise to the results
in Davy's experiments on sulphuretted hydrogen, and pro-
ved that it contains no oxygen [‡]; and any trace of hydro-
gen or oxygen in the other experiments is probably to be

[*] Journal de Physique, April 1807.
[†] Philosophical Transactions, 1809.
[‡] Recherches Physico-Chimiques, tom. i, p. 187.

referred to the influence of adhering moisture. Berzelius found, with regard to the one which would be most conclusive, the evolution of hydrogen in the mutual action of sulphur and metals, that there is no such result when the sulphur is perfectly dry.

Sect. II.—*Of Sulphuric Acid.*

THIS acid is the product of the saturation of sulphur with oxygen. To obtain it different processes have been employed. Formerly it was procured from sulphate of iron ; this salt, prepared from the decomposition of native sulphuret of iron by exposure to air and moisture, being dried and exposed to a strong heat in earthen retorts. The acid is expelled, and condensed in receivers connected with the retorts ; the portion which first distils over is weak, but it becomes more concentrated, as the process goes on, and towards the end the matter is even frequently obtained concrete, forming a substance known to the older chemists by the name of Glacial Oil of Vitriol.

Besides this process, which is not now followed in this country, though sometimes employed in Germany, the chemists often attempted to obtain sulphuric acid by the combustion of sulphur. The attempt could not be said to be successful, the product of the combustion of sulphur in atmospheric air being principally sulphurous acid, which is not easily condensed, or brought to the state of sulphuric acid : but the method was at length rendered practicable, chiefly by adding to the sulphur a portion of nitre, and burning the mixture and condensing the product, not in glass, but in vessels of lead.

This process, first established by Dr Roebuck [*], and now so successfully conducted on a large scale, consists in mixing sulphur in powder with from one-eighth to one-tenth its weight of nitrate of potash. A quantity of this mixture being put within a large leaden chamber, is kindled, the door of the chamber being closed. The sulphur, from the oxygen afforded partly by the atmospheric air, and partly by the nitric acid of the nitrate of potash, continues to burn, and the sulphuric acid formed is absorbed by water in the bottom of the chamber. The nitre is indispensable in the process, yet it is only within these few years that the theory of its action was understood. It was supposed merely to communicate oxygen to the sulphur, and thus to sustain the combustion, and enable it to proceed in close vessels, better than could be done by a supply of atmospheric air. Its operation, however, is more complicated; and the just theory of it appears to have been first suggested by Clement and Desormes [†]. The quantity of oxygen which the nitre can afford is very inconsiderable, not above $\frac{1}{50}$th of what is required, and not more indeed, as Mr Dalton has remarked, than what is necessary for the quantity of sulphuric acid, which the potash, which is its base, saturates. But in its decomposition during the slow combustion, by the partial abstraction of oxygen from the nitric acid, nitric oxide gas is evolved; this rising in the chamber combines with the oxygen of the air, and forms nitrous acid vapour, and this, aided by the watery vapour present, acts on the sulphurous acid gas, which is the product of the combustion of the sulphur, imparts to it oxygen, and thus converts it into sulphuric acid. By this abstraction of oxygen, the nitrous acid returns to the state of nitric oxide gas, which again acts in a similar manner, serving as it were as the medium

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[*] Edinburgh Philosophical Transactions, vol. iv, p. 69.

[†] Annales de Chimie, t. lix, or Nicholson's Journal, vol. xvii.

of communication of oxygen to the sulphurous acid. For this mutual action the presence of water is necessary, for the two gases dry do not act on each other; the aqueous vapour diffused through the chamber probably in a great measure favours it. If the quantity of water, however, is small, the compound formed from that action condenses in a kind of crystalline deposite, and when more water is added, is resolved into sulphuric acid, and nitric oxide gas. And Sir H. Davy has supposed that this action also goes on at the surface of the water. This theory gives the explanation of the necessity of nitre in the process, and of the failure of all attempts to withdraw or diminish it beyond a certain extent, as in no other mode could the sulphurous acid, which is the direct product of the combustion, be converted into sulphuric acid. The nitric oxide gas, it is obvious, is in part restored by the communication of oxygen from the nitrous acid vapour to the sulphurous acid, and can again take oxygen from the air, so that the process might be supposed to continue from a limited portion of it, but a fresh portion is necessary to compensate the unavoidable loss.

The sulphuric acid formed in this process, with a portion of sulphurous acid, are absorbed by water placed in the bottom of the chamber. At the end of a few weeks the liquor is drawn off, and is concentrated, first by heating it in leaden vessels, and afterwards by boiling it strongly in glass retorts. The acid is also purified by this boiling, the sulphurous acid receives oxygen, probably from a portion of nitric acid present; the liquid, from being of a brownish colour, becomes colourless; it acquires an oily consistence, and a specific gravity of about 1.842.

Though the acid, prepared in this way, is sufficiently adapted to the purposes to which it is applied in the arts, it is not quite pure. It always contains a little sulphate of potash, formed from a portion of the potash of the nitre having been dissolved by the sulphuric acid. The pre-

sence of this is rendered evident by diluting it with water; after the heat produced by the combination is diminished, the fluid is more or less cloudy, and, on standing, deposites a precipitate, consisting principally of sulphate of potash. There is reason to believe, that it consists in part, too, of sulphate of lead, derived from the vessel in which it has been prepared. Meyer has affirmed, that in diluting 22 ounces of the concentrated acid with an equal weight of distilled water, 6½ grains of a white powder were obtained, which, fused with borax, gave three grains of lead [*]; but in this experiment the quantity is undoubtedly exaggerated. By dilution with water, the acid is in a great measure freed from these substances, and it can be again concentrated, by exposing it to a strong heat in a glass retort. To render it perfectly pure for delicate chemical investigations, it is necessary that it should be distilled, a process which is attended with difficulty, from the density of the acid, and the high heat that is necessary. It is best done by exposing the retort coated with clay to an open fire, supported by a ring, instead of placing it in a sand-bath, as in this way the heat is equally applied, and the vapour is formed at the surface.

It has been found difficult to determine the proportions of the constituent principles of this acid, owing partly to sulphurous acid being formed, in any experiment in which the direct combination of its constituent parts is effected, and partly to the difficulties attending the modes of estimating the quantity of real acid produced.

The method that has been chiefly employed is one which appears to have been first employed by Berthollet, distilling nitrous acid repeatedly from sulphur, and thus, by imparting oxygen, converting it into sulphuric acid; then estimating the quantity of acid formed from a given weight of sulphur, by combining it with barytes, finding

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[*] Annales de Chimie, tom. vi. p. 30.

the weight of the sulphate, and from its known composition finding the weight of the acid. As the average result, he fixed the proportions in real sulphuric acid at 72 of sulphur, and 28 of oxygen [*].

The same method was employed by Chenevix, who fixed the proportions at 61.5 of sulphur and 38.5 of oxygen [†]; and by Thenard, who assigned those of 55.56 sulphur, and 44.44 oxygen [‡]; while the researches of Klaproth, Richter and Bucholz, of which an abstract is given in a memoir on this subject, (*Annales de Chimie*, t. lviii, p. 122,) agreed in the result of 42 or 42.5 of sulphur with 58 or 57.5 of oxygen.

These differences arise principally from the mode of determining the quantity of sulphuric acid formed, by combining it with barytes, and calculating from the proportions of the elements of sulphate of barytes, which were not accurately ascertained. The presence of water in barytes in a considerable proportion was then not known; and when the sulphuric acid was combined with the hydrate of barytes, and the weight of it in the product inferred on the supposition that it had been combined with real barytes, the proportion of the latter was stated too high, or, in other words, that of the acid too low. In the first results, the sulphate of barytes was supposed to contain from 74 to 76 of barytes in 100 parts; in the others the proportion was taken at 67 or 66, which is nearly the true estimate, and making this correction, the differences in the proportions assigned to the elements of the acid nearly disappear; those of Berthollet, with this correction, being 42 of sulphur and 58 of oxygen, which correspond nearly with the others. Berzelius, by a careful analysis, conducted by converting sulphuret of lead into sulphate of

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[*] Mémoires de l'Acad. des Sciences, 1782, p. 602.
[†] Transactions of the Irish Academy, vol. viii.
[‡] Annales de Chimie, tom. xxxii, p. 266.

lead by the action of nitric acid, gave as the proportions 40.58 of sulphur and 59.42 of oxygen; or, by another result, 39.92 of sulphur and 60.08 of oxygen, whence he inferred, that it might be stated in round numbers at 40 of sulphur and 60 of oxygen, or 100 to 150 *. There is one consideration which proves that this is just. In sulphurous acid the proportion is that of 100 of sulphur to 100 of oxygen, and the proportion of 100 to 150 in the next compound, the sulphuric, is so far conformable to a regular progression.

These proportions apply to what has been called the real acid, that is, the acid such as it is supposed to exist free from water, combined with a base in a dry sulphate, such as sulphate of potash, or of lime. In its usual insulated form, it is held to contain combined water, an opinion inferred from the fact, that when in its highest state of concentration it is combined with a base, which cannot itself afford water, a portion of water is obtained. The quantity has been variously estimated, but appears to be fixed with sufficient precision, in acid of the specific gravity 1.850, at 18.5 in 100 parts.

The view which I have proposed with regard to the constitution of acids supposed to contain combined water, is of course to be applied to this particular case. The water which sulphuric acid affords is formed in those cases in which it is obtained, and the acid itself is a ternary compound of sulphur, oxygen and hydrogen: the proportions, according to the above estimate, being 32.6 of sulphur, 65.2 of oxygen and 2.2 of hydrogen.

This obviates a difficulty which exists in the relation of the proportion of oxygen in the two compounds, sulphurous and sulphuric acids, according to the common doctrine that they are both binary compounds. In the first, 100 of sulphur are combined with 100 of oxygen; in the

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* Philosophical Magazine, vol. xli, p. 84, 345, 346.

second it is to be expected, in conformity to the common law of multiples, that 100 of sulphur will be combined with 200 of oxygen. But the quantity is only 150: And in the atomic theory this involves the absurdity, that while the first compound consists of 1 atom with 1, the second is that of 1 atom with $1\frac{1}{2}$. To obviate this, the existence of another compound of sulphur and oxygen, an oxide of sulphur, has been assumed, composed of 100 with 50, and thus the series in the proportions of oxygen is that of 1, 2, 3. But no such compound can be obtained. The difficulty is altogether obviated in the preceding view. There is no binary combination of sulphur and oxygen in the proportion of 1 with $1\frac{1}{2}$,—real sulphuric acid, as it is called. The first compound is that of sulphurous acid, in which 100 of sulphur are combined with 100 of oxygen, and the second is that of common sulphuric acid, the ternary compound, in which 100 of sulphur are combined with 200 of oxygen, conformable to the regular law. The proportion of hydrogen to the sulphur is that which forms the binary acid compound, sulphuretted hydrogen. And it deserves notice, that the sulphur is thus combined with the proportions of oxygen and hydrogen, which separately would communicate acidity ; it is easy, therefore, to perceive how the ternary compound is possessed of so high a degree of acidity as that which distinguishes it.

It may be a question, whether any binary compound of sulphur and oxygen exists, containing more oxygen than that in sulphurous acid. The real acid supposed to exist in the dry sulphates, such as sulphate of barytes or potash, is hypothetical ; it cannot be obtained, nor is there even any conclusive evidence, that the sulphur and oxygen exist in these compounds in binary combination. The two elements cannot be combined directly so as to afford any other product than sulphurous acid ; and sulphurous acid cannot be combined with an additional proportion of oxygen : the two gases, when perfectly dry, do not act on

each other, and they form sulphuric acid only when water is admitted. Neither can sulphuric acid be brought to a higher state of concentration than that of the specific gravity 1850, which denotes the constitution expressed by the above proportions. It had been affirmed, indeed, to have been obtained at a higher specific gravity, but Kirwan could not succeed in attaining this. Dr Percival exposed to heat in a retort, until the bottom of the retort and the liquor itself appeared red, a quantity of the common sulphuric acid of commerce, having the specific gravity 1.842; the specific gravity of what remained, and which amounted to about one-third of the quantity originally employed, was 1.852, beyond which the concentration could not be carried, as what passed over towards the end of the distillation was as strong as what remained. Nor was it perfectly pure, as it let fall a quantity of a white powder when diluted with water. The acid which had distilled over bore dilution without having its transparency impaired; it could not be concentrated farther than the specific gravity 1.846. And when acid is obtained by concentration of a specific gravity above 1850, it always is so from impurity, generally from the presence of sulphate of potash or sulphate of lead.

Sulphuric acid, however, can be procured in a solid or congealed state, forming what the older chemists named Glacial Oil of Vitriol. The first method employed to obtain this acid, and which has continued to be followed, in Germany particularly, is to expel it by heat from the green vitriol of commerce, the sulphate of iron. When this salt is previously dried so as to expel its water of crystallization, on submitting it to a very high heat in earthen retorts, sulphuric acid distils over, partly in the liquid state; but there condenses also in the receiver, or neck of the retort, a soft crystalline deposite, highly fuming, and which, when left exposed to the air, absorbs water, and passes at length into common sulphuric acid. This may be supposed to be the real acid free from water, or at least to be

more highly concentrated than sulphuric acid in its usual state.

It was known, that sulphurous acid gas added to sulphuric acid renders it capable of congealing at a natural temperature. Such an impregnation may be considered very likely to occur in the process now described, from the effect of the high temperature ; for sulphuric acid, by transmission through an ignited tube, is partially decomposed and converted into oxygen and sulphurous acid gases. And it was accordingly affirmed by Fourcroy, that the glacial acid from green vitriol gives fumes of sulphurous acid, and that when deprived of this acid it becomes liquid *.

Some late investigations, however, are in opposition to this, and lead rather to the opinion, that the acid in this state is sulphuric acid free or nearly so from water. Vogel has affirmed, that it contains no sulphurous acid, nor can it be formed by combining this acid with sulphuric acid : and it attracts no oxygen from the air. When mixed with water it is converted into common sulphuric acid ; and when combined with salifiable bases it forms common sulphates. It dissolves, he admits, a portion of sulphur, acquiring a green, brown, or blue colour, according to the quantity. Dobereiner has farther stated, that a given weight of this acid, diluted with water and precipitated by barytes, affords the same quantity of sulphate of barytes as is equivalent to what would be formed by real sulphuric acid †.

This question as to the nature of this product is not completely investigated ; and Vogel himself advances nothing more than a very vague hypothesis with regard to it,—that it is sulphuric acid with some imponderable substance increasing its acidity. There is an improbability in the supposition, that real sulphuric acid should be obtain-

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* Mémoires de l'Acad. des Sciences, 1785.
† Annales de Chimie, t. lxxxiv, p. 266.
  Annals of Philosophy, vol. v, p. 28. ; vol. vii, p. 34.

ed by this process, when it cannot be procured by any other: while there is every probability, from the nature of the process, that the acid distilled over may receive an impregnation of sulphurous acid, or of sulphur which it may hold in solution : And this may explain all the results; for with regard to the most conclusive of them,—the forming common sulphuric acid from an addition of water, and forming with bases real sulphates, the water added in the first case, and necessarily present also in the second, may communicate the proportions of oxygen and hydrogen necessary to convert the dissolved sulphur, or condensed sulphurous acid into sulphuric acid; and the acidity of course will be augmented, so as to be equal to what it would be supposing the original substance to be real acid. It is also possible that this glacial acid may be a ternary compound, containing hydrogen in the proportion which constitutes super-sulphuretted hydrogen, and oxygen in the proportion which is intermediate between that in sulphurous, and in sulphuric acid; though the other seems to be the more probable opinion.   When exposed to a gentle heat, it is volatilized, leaving towards the end a portion of liquid acid.   What is condensed is a kind of crystalline substance of fibrous texture, similar to asbestos, very dry and tough, fuming strongly on exposure to the air. It remains solid at a temperature of 60; but above that it takes the form of a colourless transparent vapour, which condenses on coming into contact with a humid atmosphere.

Sulphuric acid of the specific gravity 1850, or, what is the more usual strength, 1846, is of an oily consistence and appearance, inodorous, colourless and transparent, but liable to acquire a brown tinge from the smallest quantity of carbonaceous matter.   It possesses in an eminent degree all the properties of an acid.   Even when diluted with 20 or 30 parts of water, its taste is extremely sour, and it reddens instantly the vegetable colours.

It is highly corrosive, so as to erode any animal or vege-
table matter.

Sulphuric acid is capable of congealing by cold, under-
going even a regular crystallization. Its freezing point is
different, according to its state of concentration, and on
this subject there are some rather singular facts. D'Ayen
had observed that the concentrated acid congealed when
exposed to a cold of — 13° Reaumur ; that when mixed
with two or more parts of water, it could not be frozen ;
but when very much diluted it froze, a portion of the wa-
ter probably being congealed. These experiments were
confirmed by Guyton, who observed, too, that the concen-
trated acid, when congealed, remained in that state at a
less cold than that necessary to freeze it. Mr Macnab, in
his experiments at Hudson's Bay, found that sulphuric
acid of the specific gravity 1843, congealed at —15° of
Fahrenheit, while the same acid, diluted with rather more
than half its weight of water, required to congeal it a cold
of —36°, and, when further diluted, required more intense
colds. In these experiments, only a portion of the acid
congealed ; but on separating the liquid part from this,
both were found of nearly the same strength. The sub-
ject was afterwards investigated by Mr Keir *, who found
that there is a certain point of strength of the acid, at
which it congeals most readily. This is when the acid is
of the specific gravity of 1780 ; at this, or in the interme-
diate states of dilution, to 1786 on the one hand, or 1775
on the other, it freezes when exposed to the cold of melt-
ing snow ; and when more diluted or more concentrated,
the freezing required proportionally a lower temperature.
Mr Keir observed, too, the singular fact taken notice of
by Guyton, that the acid remained congealed at a higher
temperature than that necessary to congeal it. The above
diluted acid, for example, could not be congealed by a

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* Philosophical Transactions, vol. lxxvii, p. 267.

temperature above 32°; but when congealed by sur-
rounding it with melting snow, it remained solid at
higher temperatures, and when it began to melt, a ther-
mometer immersed in it indicated 45° of Fahrenheit; or
if cooled, as it might be by avoiding agitation, to 29°, on
agitating it, it instantly congealed, and the temperature
rose to 46°. The figure of the crystals is that of a six-
sided prism bevelled at both extremities, or acuminated
by six planes: the crystals are often large and hard; they
are more heavy than the part which remains liquid. Mr
Keir also observed, that the congealed portion contained
a number of air bubbles

Sulphuric acid boils, according to Bergman, at 540°;
according to Dalton at 590°; and condenses unchanged.
By passing it through an ignited tube, it is decomposed
and resolved into oxygen and sulphurous acid gases with a
portion of water *.

The attraction of this acid to water is extremely strong;
it is always found combined with it, and cannot by any
process be entirely separated from it. When exposed to
the atmosphere, it attracts watery vapour rapidly, so as
soon to increase in weight. In the course of a month, if
it has been freely exposed, its weight will be doubled; the
farther absorption becomes then more slow, until the e-
quilibrium is arrived at, between the attraction of the acid,
and the tendency of the water to pass into the elastic form.
When the concentrated acid and water are directly mix-
ed, they combine in every proportion, an increase of den-
sity and a production of heat attending the combination.
The increased density, or the deviation from the mean den-
sity, is greater as the acid is in larger proportion to the
water. The production of heat is also greater. From
mixing two parts of concentrated acid with one part of
water, Gadolin found the elevation of temperature equal
to 203 degrees of Fahrenheit; equal parts produced a rise

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* Mémoires de la Société d'Arcueil, t. i, p. 242.

equal to 175°, and from one part of acid with two of wa-
ter the rise was 108°. This increase of temperature is
owing to a diminution of capacity, as was experimentally
proved by Gadolin. When the acid is added to ice or
snow, it melts it rapidly ; and from the absorption of ca-
lorie by the liquefaction of the ice, there is a considerable
reduction of temperature ; this, however, is counteracted
to a certain extent by the heat arising from the condensa-
tion, and hence the cold is greater when the acid is pre-
viously diluted with a portion of water.

The following short table by Mr Dalton gives the spe-
cific gravities of the mixtures of sulphuric acid and water
in different proportions. It is so far hypothetical as re-
ferring to what is called real sulphuric acid as the stand-
ard; but as this represents the state in which the acid may
be conceived to exist in its saline compounds, it may have
some advantage. Dr Henry has remarked, that an ap-
proximation to the proportions, referred to sulphuric acid
in its usual state of concentration, may be obtained, by
increasing the numbers in the table indicating the real
acid one-fourth. Thus acid of the specific gravity 1.200
contains 20 *per cent.* of real acid, which increased one-
fourth, gives 25 *per cent.* of acid of 1.849.

Specific gravity.	Acid per cent. by weight.	Specific gravity.	Acid per cent. by weight.	Specific gravity.	Acid per cent. by weight.
unknown.	100	1.819	72	1.699	62
1.850	81	1.810	71	1.684	61
1.849	80	1.801	70	1.670	60
1.848	79	1.791	69	1.650	58.6
1.847	78	1.780	68	1.520	50
1.845	77	1.769	67	1.408	40
1.842	76	1.757	66	1.30+	50
1.838	75	1.744	65	1.200	20
1.833	74	1.730	64	1.10—	10
1.827	73	1.715	63		

Sulphuric acid does not form any combination with the
simple gases. Giobert had stated some experiments, par-
ticularly that of distilling it from black oxide of manganese,

to prove that a combination of it with oxygen exists, forming an oxy-sulphuric acid; but these were found inaccurate or inconclusive by Vauquelin and Chenevix. Hydrogen gas appears, from Priestley's experiments, to decompose it at a high temperature, a portion of sulphur being produced by exposing the acid in a vessel with hydrogen gas to the solar light, concentrated by a lens.

Sulphuric acid absorbs nitric oxide gas, and acquires, according to Priestley, a purple colour from this impregnation. With the fuming and concentrated nitrous acid it combines, according to Gay-Lussac, and if the temperature is not high, crystals in prisms are obtained; these give out nitric oxide gas, when they are thrown into water. This compound is similar to one formed by the mutual action of sulphurous acid, nitric oxide, oxygen gases, and watery vapour. Sulphuric acid combines also with nitric acid, and Keir observed a singular property of this compound, that it dissolves silver, without dissolving copper, or almost any other metal. He proposed an acid of this kind, prepared by dissolving 1 lb. of nitre in 8 or 10 lbs. of sulphuric acid, as a cheap solvent, for separating silver from plated copper [*].

The simple inflammables decompose sulphuric acid. When exposed to heat with charcoal, its oxygen is partially abstracted, and sulphurous acid gas and carbonic acid gas are rapidly discharged. If mixed with any vegetable or animal matter, it acquires a brown colour, a change apparently owing to the hydrogen of the vegetable matter attracting partially the oxygen of the acid, and to a portion of charcoal being evolved; hence, if heat be applied to an acid coloured, from this cause, the colour is discharged, the charcoal being converted into carbonic acid, which is expelled. The addition of a little nitrous acid has the same effect, obviously by the same agency. If the vegetable substance be one containing much hydrogen;

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as, for example, if one of the volatile oils be added to the acid, the mutual action becomes rapid even in the cold ; the mixture becomes black ; the temperature rises, sometimes even so high that the oil is inflamed, and sulphurous acid and carbonic acid gases are extricated. If the proportion of vegetable matter be small, so as to admit of the application of a moderate heat, the abstraction of oxygen from the acid is complete. This was long ago observed by Boyle, who obtained sulphur from the distillation of sulphuric acid and oil of turpentine.

Sulphur boiled with sulphuric acid receives oxygen ; and if a due proportion be observed, may be converted into sulphurous acid. Phosphorus, with the aid of a high temperature, produces a similar decomposition.

Sulphuric acid is decomposed by the greater number of the metals at a high temperature ; they attract its oxygen partially, and disengage sulphurous acid, the metallic oxide combining with the remaining acid. If diluted with from 4 to 7 parts of water, the action is different ; the metal does not decompose the acid but the water, attracting its oxygen, and disengaging the hydrogen ; the metallic oxide combines with the acid, and remains in solution. This solution proceeds rapidly even in the cold, but is confined to those few metals which have a strong attraction to hydrogen, as iron and zinc ; copper is affected in a similar manner, though more slowly. The nature of this action has been already explained, (vol. i, p. 117.)

Sulphuric acid combines with the alkalis, earths, and metallic oxides, forming the salts named Sulphates. It has been supposed to have a stronger attraction to bases than the other acids have, both as its salts are decomposed with more difficulty than the others, and as it decomposes, at least when aided by a high temperature, a number of the other neutral salts, disengaging their acid ; but this is owing, not so much to the predominant strength of affinity, as to its greater comparative fixity. In the humid way,

the decompositions it produces, like those of the other acids, are often partial, and influenced by proportion, cohesion, and other external forces. Barytes forming with this acid a very insoluble compound, all the sulphates give a copious precipitate with barytic water, or muriate or nitrate of barytes, a test by which they are recognised. They are decomposed by exposing them to heat with carbonaceous matter, which attracts the oxygen of the acid; a portion of sulphur remains in combination with the base; and by this chemical character they are particularly distinguished. They are in part also decomposed by heat alone. With regard to this, Gay-Lussac has established certain general conclusions *. All the metallic sulphates are decomposed by heat, with results which depend on the affinity of the base to the acid. Those in which the acid is little condensed, give, by distillation, sulphuric acid: those in which it is retained more strongly, and which are insoluble, give sulphurous acid and oxygen. Those which form a medium between these, and which are acidulous and soluble, give sulphuric acid, sulphurous acid and oxygen. All the earthy sulphates, which have an excess of acid, are decomposed by heat, giving sulphuric acid, oxygen gas, and sulphurous acid. The neutral alkaline sulphates are not decomposed by heat, with the exception of sulphate of ammonia; but when they are crystallized with an excess of acid, part of that excess is by heat converted into sulphurous acid and oxygen. These decompositions require a high temperature; and at a lower temperature the reverse combinations, he has shewn, are established. Thus, if a metallic sulphuret, or even an earthy or alkaline sulphuret, be roasted with a low red heat, the air being admitted, sulphuric acid is formed, and of course a sulphate is produced; but by raising the temperature higher, this sulphate is decomposed,—a fact of importance in practical chemistry, both as relating to the preparation of cer-

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* Mémoires d'Arcueil, tom. i, p. 215.

tain sulphates on a large scale, and to the roasting of metallic ores, which contain sulphur.

The determination of the composition of the sulphates is usually effected by means of barytes, muriate of barytes being added to the solution of a given weight of the salt, as long as any precipitate is thrown down. This is washed and dried at a red heat ; it is sulphate of barytes, 100 of which are equivalent to 34 of acid. The quantity of acid is thus obtained from its weight. If the loss of weight from the expulsion of water of crystallization of the salt has previously been found, the remainder gives the weight of the base, and of course the composition of the salt.

The remaining combinations of sulphuric acid fall to be considered under the history of the substances to which they belong. The acid itself is of very extensive use. It is one of the most important agents in chemical investigations, either by the affinities it directly exerts, or by the oxygen it communicates. In the arts it is much used ; particularly in bleaching ; in some of the processes of dyeing ; in some metallurgic operations ; and in the preparation of a number of the neutral salts.

Sect. III.—*Of Sulphurous Acid.*

This acid had been known to the earlier modern chemists, and in some of its combinations had been examined by Stahl. Priestley shewed that it is a permanently elastic fluid. Berthollet pointed out its relation to sulphur and sulphuric acid * ; its chemical relations were more fully investigated by Fourcroy and Vauquelin † ; and by Dr

* Mémoires de l'Acad. des Sciences, 1782, p. 597.
† Annales de Chimie, tom. xxiv ; or Nicholson's Journal, 4to, vol. i, p. 313.

Thomson [*], and its composition has been determined by Davy and Gay-Lussac.

Sulphurous acid is obtained by the combustion of sulphur, but it is mixed with a little sulphuric acid, and it is not easy to conduct the process so as to obtain it pure. It is procured, therefore, rather by decomposing sulphuric acid by the action of substances which partially abstract its oxygen, and which do not form an aëriform product. The metals answer to this character; those should be employed which do not decompose water, as from the portion of water which the sulphuric acid contains, a little hydrogen gas might be evolved. Quicksilver, or tin, on the whole, answers best. One part of either is put into a retort, with two parts of sulphuric acid; heat is applied by a lamp, the metal attracts part of the oxygen of the acid, and the sulphurous acid gas, as it is condensed by water, is received over mercury.

The composition of sulphurous acid had been variously determined, as to the proportions of its constituent parts. There is some difficulty in conducting the direct synthetic experiment, but there is reason to believe, that oxygen gas, in combining with sulphur to form sulphurous acid gas, undergoes no change of volume, its density being merely augmented by that of the sulphur. Gay-Lussac found, that in heating sulphuret of mercury in 100 measures of oxygen gas, 93 measures of sulphurous acid gas were formed[†], and this condensation might have arisen from the production of a little sulphuric acid. Sir H. Davy obtained a similar result. In burning sulphur in dry oxygen gas the volume was very little altered; the condensation never being more than $\frac{1}{12}$, and seldom so much as $\frac{1}{15}$; and it might be ascribed, he supposed, to a little hydrogen attached to the sulphur. The conclusion, that there is no

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[*] Nicholson's Journal, vol. vi, p. 93.
[†] Mémoires d'Arcueil, tom. ii, p. 221.

change of volume from the combination of the sulphur,
was confirmed by experiments on the action of sulphur,
or sulphuret of mercury on metallic oxides, red oxide of
mercury, for example, which yields oxygen, affording the
same volume of gas nearly when heated with sulphur, as
when heated alone *. It is obvious, from this result, that
the proportion of sulphur may be determined from the dif-
ference in specific gravity between sulphurous acid gas and
oxygen gas, subtracting the former from the latter. Cal-
culating from this, Gay-Lussac inferred, according to the
specific gravity of the former gas assigned by Kirwan, that
it is composed of 100 of sulphur with 95 of oxygen, or
51.3 with 48.7. But from a more accurate estimate of the
specific gravity, the proportions, as Davy remarked, will
be equal weights. Berzelius, by a different mode of inves-
tigation,—converting a sulphite into a sulphate by the
agency of nitric acid, obtained as the proportions 50.6 of
sulphur and 49.4 of oxygen †, an approximation sufficient-
ly nigh to justify the conclusion that they are equal parts.
And this is lastly confirmed by the proportions in sulphu-
ric acid, already stated, which are conformable to those of
1, and 1 in sulphurous acid, according to the law of multi-
ples observed in chemical combinations.

This acid is gaseous, but it has, by intense cold and
strong pressure, been reduced to the liquid state : this was
effected by Monge. Mr Northmore, by pressure alone,
succeeded in condensing it into a thick fluid of a dark yel-
low colour, which immediately evaporated on the removal
of pressure ‡. How far this may have been aided by the
presence of hygrometric vapour is uncertain. In its ga-
seous state its specific gravity is stated by Kirwan at 2.24;
by Davy, with more accuracy probably, at 2.193, or by

* Chemical Philosophy, p. 274.
† Philosophical Magazine, vol. xli, p. 89.
‡ Nicholson's Journal, vol. xiii, p. 236.

subsequent experiments a little higher[*] ; by calculation it is 2.222. 100 cubic inches weigh between 67 and 68 grains. It has a suffocating pungent odour, proves speedily fatal to life, and instantly extinguishes combustion.

It appears to be decomposed by heat, and to be resolved into sulphur and sulphuric acid. The production of sulphur was observed by Priestley, from exposing its aqueous solution to heat in glass tubes hermetically sealed. Vauquelin also observed the deposition of sulphur, and the production of sulphuric acid, by passing the gas through a tube at a red heat[†]. Moisture probably must have been present.

Sulphurous acid is absorbed by water : 100 grains of water take up 5 grains of the gas; or, according to Dr Thomson, 8.2 grains, equal to 33 times its volume. The solution has a pungent disagreeable odour, and an acid taste. It reddens some of the vegetable colours, such as that of litmus or red cabbage ; there are others, the colour of which it destroys, as that of the red rose : and the colour in the greater number is impaired by it. Syrup of violet reddened by an acid has been affirmed to have its blue colour restored [‡]. The acid, in its gaseous form, acts with still more energy in destroying colour, and it hence whitens some animal substances.

The saturated solution allows the gas to escape at a moderate heat, and by boiling, the greater part is expelled, though the liquor remains acid, apparently from the presence of sulphuric acid. It is singular that it is not expelled by freezing ; it remains combined with ice, and renders it so heavy that it sinks in water. This fact shews that this gas has, comparatively with others, little tendency to pass into the aëriform state. The freezing of the solution takes place at a few degrees below 32.

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* Philosophical Transactions, 1810—1812.
† Journal de l'Ecole Polytech. Cah. II, p. 183.
‡ Nicholson's Journal, vol. xvii, p. 303.

The liquid sulphurous acid slowly absorbs oxygen from the atmosphere, and is converted into sulphuric acid.

When two parts of it in the state of gas are mixed with one part of oxygen gas, if the mixture is kept dry, they do not act on each other. But if a small portion of water is introduced, they gradually combine and form sulphuric acid, a result depending on water or hydrogen being necessary to the constitution of sulphuric acid in its insulated state. By passing a mixture of oxygen gas and sulphurous acid gas through a tube heated to redness, sulphuric acid is said to be formed; probably, however, only partially, and so far as hydrogen or moisture is present. Sulphuric acid, transmitted through an ignited tube, is converted, as has been already stated, into sulphurous acid and oxygen gases; or at least affords a certain portion of these products.

Hydrogen does not act upon this acid at a low temperature, but at ignition it attracts its oxygen; on passing a mixture of the two through a red-hot tube, the sulphur partly combines with a portion of hydrogen, and is partly deposited. Charcoal produces a similar change; by passing sulphurous acid over ignited charcoal, carbonic acid is produced, and sulphur is deposited. It is not decomposed by phosphorus, and it acts feebly on the metals. It decomposes nitric acid, by attracting part of its oxygen, passing to the state of sulphuric acid, and converting the nitric into nitrous. Nitric oxide gas does not act on it if water is excluded; neither does nitrous acid vapour; but if to the latter mixture a little water be admitted, a solid crystalline deposite is formed; and if more water be added, nitric oxide gas is given off, and the sulphurous is converted into sulphuric acid. Sulphurous acid gas is absorbed by sulphuric acid, and a soft crystalline substance is formed.

This acid combines with the alkalis, forming salts named Sulphites. Their taste is sulphureous; they are de-

composed by a high temperature, their acid being expelled, or a portion of sulphur being driven off, in which case they become sulphates ; they are also decomposed by the greater number of the acids, the sulphurous acid being disengaged with effervescence ; the alkaline sulphites are more soluble than the sulphates in water, the earthy sulphites less so. They are converted into sulphates by exposure to the air, or by the action of substances affording oxygen.

According to Gay-Lussac, sulphuretted sulphites, that is, compounds of alkaline bases with sulphurous acid and sulphur, may be formed, and have all the properties of neutral salts. If a solution of sulphuret of strontites be left exposed to the air it loses its colour in a few days, and usually a precipitation of sulphur and of carbonate takes place. The liquor submitted to evaporation affords very fine rhomboidal crystals, perfectly neutral, having a faint sulphureous taste, soluble in water, and which do not suffer any change from exposure to the air, except losing at a temperature above 120° a portion of water. This salt is decomposed by heat, gives out sulphur, and leaves a sulphate and sulphuret. The solution of sulphuret of lime affords by the same method a similar salt crystallized in prisms, rather more soluble in water, and which suffers no alteration from exposure to the air *. The precise constitution, however, of these compounds does not appear to be very well determined. Gay-Lussac points them out as affording an exception to the principle which has been maintained that acidity is proportional, not to the oxygen in an acid, but rather to its radical, a principle supported by the fact, that a sulphite is converted by oxygenation into a sulphate without any change in the state of neutralization. According to Gay Lussac, however, if a sulphuretted sulphite receive oxygen, it is not converted into a

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* Annales de Chimie, tom. lxxxv, p. 199.

neutral sulphite or sulphate; for on oxygenating the sulphuretted sulphite of strontites by nitric acid, and removing the precipitate of sulphate formed, on pouring into the liquor muriate of strontites, a new precipitation was produced, very abundant. And the same result was obtained with the sulphuretted sulphites of barytes and lime. Gay-Lussac states, that a sulphite can dissolve a portion of sulphur. On boiling a solution of sulphite of potash with potash, a large quantity of sulphurous acid is disengaged, and the sulphuretted sulphite which is formed is still neutral. This fact at least proves, that in these combinations sulphur neutralizes the alkaline properties, while the other result would appear to prove that a larger quantity of it is required to do so, than when it is combined with oxygen in the state of sulphuric or sulphurous acid. The whole subject, however, would require farther experimental investigation.

Sect. IV.—*Of Sulphuretted Hydrogen, or Hydro-Sulphuretted Acid.*

SULPHUR combines with hydrogen in different proportions. There is one compound existing in the elastic form, usually named Sulphuretted Hydrogen. And another, in which the proportion of sulphur is larger, has been obtained in the liquid state, which may be distinguished by the appellation of Super-sulphuretted Hydrogen. The history of the first of these compounds is the subject of the present section.

The term Sulphuretted Hydrogen denotes sufficiently the constitution of this compound, and in this respect is unexceptionable. But the compound is possessed of

unequivocal acid powers, and in conformity therefore to analogy from other acids, its name ought to have a relation to this. It contains, however, no oxygen, and hence the usual nomenclature cannot be applied, and there is considerable difficulty in finding a proper appellation. Gay-Lussac has named it Hydro-sulphuric acid; but this name is very objectionable; it denotes sulphuric acid with some relation to hydrogen or to water; it has even been already applied to sulphuric acid in its common state, containing, according to the common doctrine, combined water: and it is not easy to form proper names of its salts bearing a relation to the term. I have already, in explaining the nomenclature of acids, offered some observations on this subject. To introduce the terms I have suggested might be too great an innovation: And it is less necessary in the present case, as a name may be provisionally applied to sulphuretted hydrogen free from any objection. It may be named Hydro-sulphured, or, to deviate less from common usage, Hydro-sulphuretted acid, thus denoting both its constitution and its relation to acidity; and having the farther advantages, that the generic name already applied to its salts, that of Hydro-sulphuret, may be retained.

This compound was discovered by Scheele. Bergman and Kirwan prosecuted the investigation of its properties. Gengembre seems first to have shewn that it is a compound of sulphur and hydrogen, and that it owes its origin to the decomposition of water in the processes by which it is formed. It is formed in various processes, in which its elements are presented to each other in a nascent or a condensed state.

That which succeeds best is applying diluted muriatic acid to the compound of sulphur and iron. This compound is prepared for this purpose by exposing to heat, in a covered crucible, a mixture of one part of sulphur in powder with three parts of iron-filings by weight, until the

sulphur is fused and unites with the iron.   The sulphuret
of iron, when cold, is easily reduced to powder; one part
of this is put into a matrass, to which a bent tube is adapt-
ed; and two parts of muriatic acid, previously diluted with
four parts of water, are poured upon it; sulphuretted hy-
drogen gas is soon disengaged, and may be received over
water, as it is not immediately largely absorbed.   In this
process the acid, by a disposing affinity, enables the iron
of the sulphuret of iron to decompose the water, by at-
tracting its oxygen; the hydrogen is disengaged, and be-
ing presented in its nascent state to the sulphur of the sul-
phuret, combines with it, and forms the sulphuretted hy-
drogen, which passes into the elastic form.   It has been af-
firmed, that a portion of uncombined hydrogen is also dis-
engaged, and mixes with the sulphuretted hydrogen gas.
The quantity of this, however, is inconsiderable.   Mr Dal-
ton states, that the sulphuret of iron, formed by applying
to iron, which has been raised to a white heat in a forge,
a roll of sulphur, gives it more free from hydrogen.   The
most certain method of obtaining sulphuretted hydrogen
quite pure, according to Gay-Lussac and Thenard, is ap-
plying heat to sulphuret of antimony and muriatic acid;
or disengaging it from its compounds with the alkalis, by
a diluted acid.

The last process is the one which used formerly to be
followed.   When sulphur is combined with potash, soda,
or lime, on dissolving the compound in water, a partial
decomposition of the water takes place; one portion of the
sulphur combines with part of the oxygen of the water,
forming sulphuric acid, which unites with the potash; an-
other portion unites with the hydrogen, forming sulphu-
retted hydrogen, which is likewise detained by its affinity
to the alkali.   But on adding an acid to the solution, or
on adding the acid diluted to the solid sulphuret, the sul-
phuretted hydrogen gas is disengaged.   From being pro-
cured by this process, it derived the name of Hepatic Air;

the compound of sulphur and potash, from a fancied resemblance in colour to the liver of an animal, having been named Hepar Sulphuris.

This gas is also produced on exposing to a strong heat mixtures of sulphur with vegetable matter, as sugar, oil, or even charcoal, the hydrogen existing in these substances combining with the sulphur; but in these processes it is not pure.

Sulphuretted hydrogen cannot easily be formed by the direct combination of its elements. Kirwan was unable to form it by melting sulphur in hydrogen gas; and the Dutch chemists were equally unsuccessful, either by this method, or by passing hydrogen gas through a heated tube containing liquid sulphur. Scheele observed, that although by heating sulphur in hydrogen gas, the gas acquires a fœtid odour, yet it is not absorbed by water, as it would be were it converted into sulphuretted hydrogen. A small portion, however, appears to be formed. Davy found, that when sulphur is heated in hydrogen gas, part of the gas passes to the state of sulphuretted hydrogen which water absorbs. Gay-Lussac and Thenard obtained a similar result; but they add, that though they heated the sulphur in the gas a considerable time, scarcely a fifth of the hydrogen was converted into sulphuretted hydrogen [*].

The specific gravity of sulphuretted hydrogen gas was stated by Kirwan, 1.142: according to Davy it is 1.1770; and according to Gay-Lussac and Thenard 1.1912; this last appears to be most correct: 100 cubic inches weigh 36.5 grains. Its smell is extremely fœtid and peculiar. It is inflammable, extinguishes combustion, and is incapable of supporting animal life.

It is absorbed by water, the water taking up more than its volume, or 100 cubic inches absorbing, according to

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[*] Recherches Physico-Chimiques, tom. i, p. 191.

Henry, 108 ; but the quantity appears to be considerably larger. Saussure states it at 253. The water from this impregnation acquires the fœtid smell of the gas, and a nauseous taste. It is colourless and transparent. Berthollet states, in opposition to what has generally been affirmed, that this solution suffers no other change on exposure to the atmosphere than allowing the gas to escape; that when kept in a vessel of atmospheric air, the sulphuretted hydrogen suffers no decomposition ; and that it is decomposed by oxygen and its sulphur precipitated, only when it is combined with an alkaline or earthy base, which, by a disposing affinity, promotes their mutual action. Yet Kirwan has affirmed, that when dissolved in water it is decomposed : if even the water has been previously freed of air by boiling, and if the solution were kept in a bottle well stopt, and inverted in quicksilver, in a few days it became turbid, and in a few weeks deposited sulphur *.

In its elastic state, sulphuretted hydrogen does not combine with oxygen at low temperatures ; but if a mixture of it with oxygen, or atmospheric air, be placed over water, their mutual action is facilitated, the oxygen combines with the hydrogen, and a thin deposite of sulphur is formed on the vessel.

At the temperature of ignition the combination is rapid. If the sulphuretted hydrogen gas be kindled in contact with the atmospheric air, it burns with a blue lambent flame. When previously mixed with one or two parts of atmospheric air it does not detonate, and the combustion of its elements is not complete, part of the sulphur being deposited on the sides of the vessel. When mixed with an equal volume of oxygen gas, and kindled, it inflames with detonation, the products being watery vapour and sulphurous acid, though still part of the sulphur is precipitated, $1\frac{1}{2}$ volume of oxygen being necessary for the complete

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* Philosophical Transactions, vol. lxxvi, p. 129.

combustion. The action of sulphurous acid upon it is singular. If the two gases are mixed, there is a deposition of sulphur, which is derived from both of them, the oxygen of the acid combining with the hydrogen of the sulphuretted hydrogen, and forming water. Or if sulphurous acid is added to a solution of sulphuretted hydrogen in water, a similar decomposition happens, and the liquid becomes turbid, from the production of sulphur. A mixture of sulphuretted hydrogen gas with an equal measure of nitric oxide gas, burns when kindled, with a yellow or green lambent flame, and a portion of sulphur is deposited. If the proportion of nitric oxide be two to one of the sulphuretted hydrogen, their mutual action takes place, without ignition : part of the oxygen is abstracted by the hydrogen, sulphur is deposited, and the residual gas Kirwan found to be nitrous oxide. Nitrous acid poured into the gas causes its instant decomposition, a precipitation of sulphur, and a production of nitrous oxide ; or added to its watery solution also decomposes it, precipitating the sulphur.

Sulphuretted hydrogen has a peculiar action on the metals, which affords one of its most discriminating characters. If added to any of the metallic solutions, it produces a precipitate generally of a dark colour, consisting of the metallic oxide, or in some cases of the metal in combination with the sulphur. It tarnishes the surface even of the pure metals, communicating to them shades of yellow, brown or purple, with a diminution of lustre. Several of them when heated in it, tin for example, decompose it by combining with its sulphur. Potassium and sodium produce a similar decomposition, with much heat and illumination,—effects similar to the evolution of heat and light which attends the direct combination of sulphur with a number of the metals.

From some of these decompositions, the proportions of the elements of this compound have been inferred. But

a more direct analysis of it is obtained by the action of
electricity. It was known, that when decomposed by the
electric spark its sulphur is precipitated, and there is no
change of volume : and Davy found, that when formed by
heating sulphur in hydrogen gas the volume likewise re-
mains unaltered. Calculating on the specific gravity of
sulphuretted hydrogen gas being such, that 100 cubic in-
ches weigh 36.5 grains, if 2.27, which is the weight of 100
cubic inches of pure hydrogen, be subtracted, it gives 34.23
as the quantity of sulphur in the gas. According to this,
100 grains of sulphuretted hydrogen will be composed of
6.2 of hydrogen, and 93.8 of sulphur. Gay-Lussac and
Thenard found, that when sulphuretted hydrogen is de-
composed by tin being heated in it, the volume of gas re-
mains unaltered. From the specific gravity they assign,
they state the proportions at 6.145, and 93.855 [*].

The existence of oxygen in its composition was at one
time inferred, principally from the consideration that it
has the properties of an acid, and that acidity implies the
presence of oxygen. Sir H. Davy farther considered this
as established by experiments, in which the inflammabi-
lity of potassium appeared to be diminished when it had
been employed in decomposing the gas. Gay-Lussac
and Thenard pointed out the error in these experiments,
whence this conclusion was drawn; and farther shewed,
that no trace of oxygen can be discovered in its compo-
sition. It consists of sulphur and hydrogen alone, and its
acidity is no doubt developed by the agency of the latter
element, as has been already illustrated in considering the
general theory of acids.

That it has the properties of an acid, is shewn by its ex-
erting the most obvious agency of acids, that of changing
the vegetable colours, at least those which are more deli-

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[*] Recherches Physico-Chimiques, tom. i, p. 191.

cate, to a red. If paper, tinged with the infusion of lit-
mus, or with the juice of radish, be immersed in its wa-
tery solution, it is immediately reddened. If the gas it-
self is transmitted through infusion of litmus, it reddens
it ; and this, as Kirwan shewed, if it were freed from all
foreign acid by transmission through water ; or if passed
from an infusion, which it had already reddened, into ano-
ther portion of fresh infusion, it preserved the same pro-
perty [*]. It also decomposes soap, and precipitates sul-
phur from its combinations with potash or lime. And
what is the most unequivocal acid power, it combines with
the alkalis and earths, neutralizes the alkaline properties,
and forms compounds, soluble, crystallizable, and having
all the general properties of neutral salts. Some of these
results have been considered as doubtful. Though its
solution reddens some of the vegetable colours, it has been
affirmed that it renders another delicate colour, which is
reddened by the acids, the syrup of violet, green. And
Berthollet, who regards it as an acid, admits that he is
not certain " if its power is sufficiently energetic to pro-
duce the neutral state with the alkaline bases [†]." There
seems, however, to be no sufficient reason for any doubt
with regard to this; and the analogy which is now far-
ther established with regard to other acids being formed
by the agency of hydrogen, serves to confirm the conclu-
sion with regard to sulphuretted hydrogen.

The compounds of sulphuretted hydrogen, or hydro-
sulphuretted acid, as it may be named, are formed by pass-
ing a current of it in its elastic state through the alkaline
solution, or through water in which an earth is suspend-
ed. The transmission is continued until the liquor is sa-
turated ; and any excess of sulphuretted hydrogen may be
expelled by a moderate heat. They have been said to be

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* Philosophical Transactions, vol. lxxvi, p. 128.
† Chemical Statics, vol. ii, p. 86.

formed, too, by boiling sulphur with the alkali or earth in
water, or dissolving an alkaline or earthy sulphuret in wa-
ter, when from the decomposition of the water sulphuret-
ted hydrogen is formed, which combines with the alkaline
base, and by evaporation of the filtered solution, and cool-
ing, the compound may be obtained in a crystallized form;
but in these latter modes of forming these compounds
there is always an excess of sulphur.

The compounds of sulphuretted hydrogen with alkaline
and earthy bases were named by Berthollet *Hydro sul-
fures*,—a term translated into Hydro-sulphurets; and
though not strictly analogous to the generic appellations
of other salts, it might be difficult, in the present state of
chemical nomenclature, to substitute one less objection-
able. That of Hydro-sulphuride might be employed, or
of Sulphuride, or Sulphide, which I have already sug-
gested. The hydro-sulphurets of the alkalis and alkaline
earths are soluble in water, and crystallizable; the solu-
tion is colourless, while the action of the air is excluded;
but when it is admitted, a yellow colour is acquired, ow-
ing to the oxygen of the atmosphere combining with the
hydrogen of a portion of the sulphuretted hydrogen, while
the sulphur combines with the remaining portion of it,
forming a super-sulphuretted hydrogen in union with the
base. If the access of the air be permitted, oxygen con-
tinues to be absorbed, part of the sulphur is deposited, and
part converted into sulphuric acid, forming with the base
a sulphate. If to the solution of the hydro-sulphuret which
has not been acted on by the air, an acid be added, sul-
phuretted hydrogen gas is disengaged, without any depo-
sition of sulphur; while if it has been previously exposed
to the air sulphur is deposited. The saturated solutions
of the hydro-sulphurets are decomposed by boiling, part
of the hydro-sulphuretted acid escaping, and the liquor
remaining alkaline.

In acting on the metallic oxides, the hydro-sulphuretted

acid sometimes combines directly with the oxide; and, in general, these compounds are of sparing solubility, and of dark colours, so as when formed by adding an alkaline hydro-sulphuret to a metallic salt, they give dark-coloured precipitates. But more frequently, from the weaker attraction by which the oxygen is retained in the common metallic oxides than in the alkalis and earths, a mutual decomposition takes place, the hydrogen of the sulphuretted hydrogen combines with the oxygen partially or entirely, and a sulphuretted oxide, or a metallic sulphuret, is precipitated.

The properties of the individual hydro-sulphurets will be noticed under the history of their respective bases.

SECT. V.—*Of Super-Sulphuretted Hydrogen, or Hydroguretted Sulphur.*

THE compound to which, from the larger proportion of sulphur in its composition, the name of Super-sulphuretted Hydrogen has been given, and which has also received the harsher appellation of Hydroguretted Sulphur, was first observed by Scheele, and was afterwards examined by Berthollet. It is obtained by pouring small quantities of the solution of sulphuret of potash, or lime, into muriatic acid; a little sulphuretted hydrogen gas is disengaged; sulphur is precipitated; and a liquid which has the appearance of oil, of a yellow or reddish colour, gradually collects, and subsides to the bottom of the vessel. This is the super-sulphuretted hydrogen.

It appears to be very susceptible of decomposition. Sulphuretted hydrogen escapes from it even at a moderate temperature, and it is thus ultimately converted into sulphur: the same change is produced in it by the action of

the air. While it remains undecomposed, it is of a thick consistence and adhesive : its taste is hot and bitter : it appears to be decomposed by water. Mr Dalton, decomposing it by heat, found, that 30 grains yielded, after the expulsion of sulphuretted hydrogen, a residuum of 21 grains, which, when ignited, burnt entirely away with a blue flame. From the relation in the combining weights of sulphur and hydrogen, it follows, that this substance should be composed of 3.1 of hydrogen and 96.9 of sulphur; but its precise composition has not been established by experiment, as there is the difficulty of obtaining it insulated and permanent.

This substance is capable of combining with the alkalis and earths, or at least compounds are formed of these, with a combination of sulphur and hydrogen, containing more sulphur than sulphuretted hydrogen ; and the principal part of the chemical history of super-sulphuretted hydrogen relates to these combinations. They are formed by boiling an alkaline hydro-sulphuret with a quantity of sulphur, the sulphuretted hydrogen combining with the sulphur, and forming the super-sulphuretted hydrogen, which then remains in combination with the alkaline base; the liquid becomes of a darker colour. The solutions of the alkaline sulphurets in water are compounds likewise of this kind. It was known, that when dry sulphuret of potash, of soda, or of lime, is moistened with water, or dissolved in it, a decomposition of the water, and a production of sulphuric acid and sulphuretted hydrogen takes place *. The view given of the nature of these solutions was somewhat complicated. On dissolving the sulphuret in water, a portion of the water is decomposed, by the affinity of the sulphur to its principles, aided by the disposing affinity of the alkali ; the oxygen of this combining with one portion of sulphur forms sulphuric acid, with which a

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* Mémoires de l'Acad. des Sciences, 1786, p. 55.

quantity of the alkaline base enters into union ; the hydro-
gen of the decomposed water uniting with another pro-
portion of sulphur, forms sulphuretted hydrogen, with
which another portion of the alkali combines ; and thus
there exist in the liquid, it was supposed, part of the ori-
ginal sulphuret, a quantity of sulphate, and a quantity of
hydro-sulphuret of the alkali.   The view presented by
Berthollet of the nature of these solutions is more simple.
When they are formed either by dissolving the dry sul-
phuret in water, or, what amounts to the same thing, by
boiling the alkali or earth with sulphur in water, a decom-
position of the water takes place, and a portion of a sul-
phate is formed from the production of sulphuric acid, by
the union of the sulphur with the oxygen of the water.
But the sulphuretted hydrogen, also produced, instead of
being supposed to form a binary compound with a part of
the alkali, leaving a portion of the alkaline sulphuret like-
wise in the liquor, unites with the sulphur and the alkali
present, forming a compound of super-sulphuretted hydro-
gen with the alkaline or earthy base.   They have been
supposed to differ in nothing from the compounds obtain-
ed by boiling a hydro-sulphuret with sulphur, except in
containing a little of a sulphate which does not appear to
modify their properties.   They appear, however, to con-
tain an excess of sulphur, and less hydrogen, little sulphu-
retted hydrogen being disengaged, when they are decom-
posed by an acid, while much sulphur is precipitated.

These compounds * have a yellow colour, more or less

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* It is difficult to form a correct nomenclature for these
combinations of sulphur with hydrogen.   Berthollet, who first
attended to these compounds, gave to the compound with the
largest proportion of hydrogen, the name of *Hydrogéne Sul-
furé*, Sulphuretted Hydrogen ; the other he named *Soufre Hy-
drogéné*, Hydrogenated Sulphur.   The compounds formed of
the first with alkalis, earths, or metallic oxides, he named *Hy-*

deep, according to their concentration, but varying also
in their tinge from a greenish yellow to an orange red, a
fact which proves that they are not uniform in their com-
position, but differ in the proportions of their constituent
parts, principally perhaps in the proportion of the sulphur,
but probably also in the proportion of sulphuretted hydro-
gen. In proof of this, it has been remarked by Proust,
that from these liquors, prepared with different propor-
tions, and with or without the application of heat, the
quantities of sulphur precipitated, and of sulphuretted hy-
drogen disengaged by an acid, are very various *. Their
smell is slightly fœtid. They seem liable to spontaneous
decomposition, probably from the re-action of their parts,

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dro-sulfures, (Hydro-sulphurets); those of the second Sulfures
Hydrogénés, (Hydrogenated Sulphurets.) This nomenclature,
in the English translation, is not appropriate, for there is no
real distinction between hydro-sulphuret and hydrogenated
sulphuret. Mr Chenevix proposed a different nomenclature.
Retaining the term Sulphuretted Hydrogen, in its usual sense,
he gave to the other, in which there is an excess of sulphur,
the name of Hydroguretted Sulphur. The compounds of the
first he names Sulphuretted Hydrogurets; those of the second
Hydroguretted Sulphurets. These terms are systematic; but
they are uncouth, and so much alike, that when using them,
it requires some reflection to recollect the distinction between
a Sulphuretted Hydroguret and a Hydroguretted Sulphuret.
The nomenclature proposed by Kirwan, though it does not ac-
cord altogether with present views, is less objectionable. He
gave the name of Super-sulphuretted Hydrogen to that com-
pound in which there is the larger proportion of sulphur, and
its compounds he named Super-sulphuretted Hydro-sulphurets.
The prefixed syllable super may be dropt as redundant; and
we shall then have the series of sulphur, sulphuretted hydro-
gen, super-sulphuretted hydrogen; with the corresponding
names of their combinations,—sulphuret, hydro-sulphuret, and
sulphuretted hydro-sulphuret.

* Journal de Physique, tom. lix, p. 266.

as, when kept for a length of time secluded from the air, their colour becomes fainter, and sulphur is deposited. They are decomposed by the affusion of an acid which combines with the alkaline or earthy base, disengages the sulphuretted hydrogen gas, and precipitates the sulphur. This precipitated sulphur has a white colour, apparently, as has been already observed, from a small quantity of water combined with it.   It was formerly named Lac Sulphuris.

The most important chemical property of these fluids is the facility with which they combine with oxygen in its elastic state.   If exposed to oxygen gas, an absorption takes place, and continues until the greater part of the sulphur is converted into sulphuric acid.   And the effect is the same when they are exposed to atmospheric air.

The view formerly given of the nature of this absorption was complicated.   The hydrogen of the sulphuretted hydrogen was supposed to attract the oxygen of the air.   The sulphur thus separated was supposed to combine with the base with which the sulphuretted hydrogen had been combined ; a portion of sulphuret is therefore reproduced ; this reacts on the water, decomposes a new portion of it, producing, by the union of the oxygen with the sulphur, another quantity of sulphuric acid, and, by the union of the hydrogen, another portion of sulphuretted hydrogen ; and these successive changes, it was supposed, went on, until the whole of the sulphur was converted into sulphuric acid, and the liquor became a solution of sulphate.   The view given by Berthollet is more simple, and probably just. Sulphur, from its state of cohesion, is incapable of combining with oxygen at a low temperature ; in diminishing the cohesion, by raising the temperature, this obstacle is in part withdrawn, but the combination is counteracted by the heat increasing the elasticity of the oxygen gas.   When sulphur is combined with an alkali, so as to form a soluble compound, it gains the advantage of fluidity without this in-

crease in the elasticity of the oxygen. Hence, at this low temperature, their combination under these circumstances can take place with as much facility as when the sulphur is melted by heat alone; and the combination is also promoted by the affinity exerted by the alkali or earth present to each. The hydrogen of the sulphuretted hydrogen in the liquor may likewise attract oxygen, and accelerate the effect. When these liquors are long exposed to the air, it appears from the observations of Austin *, that there is an absorption of nitrogen, which combines with the hydrogen of the sulphuretted hydrogen and forms ammonia; or rather, the small portion of nitrogen gas absorbed by these in common with all watery liquids, enters in this condensed state into combination with the hydrogen.

From this property of these compounds, they have been applied to the purpose of eudiometry, and they afford the most simple eudiometer. The sulphuretted hydro-sulphuret of potash, or of lime, is employed. The former is prepared by dissolving one part of the solid sulphuret in 5 or 6 of water, or by boiling one part of sulphur with three parts of the solution of potash of the common strength, and 4 or 5 parts of water, and, after due boiling, closing the vessel, and allowing the undissolved sulphur to subside. The latter, which is rather more active, is prepared by boiling equal weights of lime and sulphur in 10 or 12 times their weight of water, for half an hour, and pouring off the liquor from the undissolved matter.

When the air is merely submitted to the action of these liquors in a narrow graduated tube, the absorption of oxygen goes on very slowly; it is only after some hours that any diminution of volume is perceived; and it requires two or three days to render the absorption complete. It was therefore a desideratum to accelerate the absorption, by using an apparatus which shall present a large surface, re-

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* Philosophical Transactions, vol. lxxviii.

newed quickly by agitation of the liquid to the air. De Marti, for this purpose, used a tube ten inches long and five lines in diameter, graduated into 100 parts : this tube being filled with water, atmospheric air is admitted so as to occupy the graduated part : this portion of air is then introduced into a flask, from two or four times the capacity of the tube, filled with the sulphuretted solution, and having a stopper adapted to it by which it can be accurately closed. The air being strongly agitated with the liquor for five minutes, is again transferred into the graduated tube filled with water, and the diminution of volume which it sustained is ascertained *.

The apparatus which Dr Hope introduced is much superior, and unites indeed every advantage. It consists (fig. 53.) of a small bottle designed to contain the sulphuretted solution ; to the mouth of this is adapted by grinding a tube divided into 100 equal parts, and towards the bottom of the bottle is an orifice fitted accurately with a stopper. The bottle being filled with the solution, and its orifice being covered with a flat plate of glass, is placed under the surface of water, and the graduated tube containing the atmospheric air, or whatever gas may be subjected to trial, is inserted into it. The apparatus is then removed from the water, is inclined so as to allow part of the liquor to flow into the tube, and agitated strongly. On withdrawing the stopper of the bottle under water a portion flows in from the absorption of the oxygen of the air. The stopper is again introduced, the agitation renewed, and the operation is repeated until the absorption proceeds no farther. The amount of this may be determined by plunging the bottle with the tube adapted to it into water, removing the stopper of the under orifice, and taking care that the water without is at the same level as the liquor within, allowing it also to stand for a short time, that any

* Journal de Physique, tom. lii, p. 177.

slight rise of temperature from the application of the hand during the agitation may have ceased. If the liquor is not highly concentrated, it is in general necessary to leave the air in contact with it for an hour or two, agitating occasionally, to obtain the full effect.

The diminution which atmospheric air suffers when subjected to this eudiometrical method, is between 21 and 22 in 100. Generally speaking, it is of easier execution, and requires fewer precautions, or corrections for error than any other; but it is less delicate than some methods, as the only diminution is that from the abstraction of the oxygen, and any error therefore in the observation becomes greater. It is also liable to some fallacy from the absorption of a little nitrogen gas. If newly prepared by boiling, and if used without previous exposure to the air, it absorbs, in common with any watery liquid, a portion of the atmospheric air decomposed, or of its nitrogen as well as of its oxygen, and probably the substances with which it is impregnated may even render the absorption of nitrogen rather greater than it would be by pure water. Accordingly, under these circumstances, nitrogen is absorbed by these liquids, and even in large quantity, when the proportion of liquid to the air is considerable. De Marti found by experiment, that a sulphuretted hydro-sulphuret of lime prepared by boiling, and cooled without exposure to the atmosphere, caused a diminution of 50 in 100 of atmospheric air, when one measure of the air had been agitated with 20 measures of the liquid [*]. Berthollet did not find this absorption of nitrogen; but he operated with a sulphuretted liquid prepared in the cold. Humboldt and Gay-Lussac, on repeating the experiment of De Marti, obtained a similar result, the absorption of nitrogen being greater, as the proportion of liquid was greater to that of the atmospheric air employed; so that in one experiment

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[*] Journal de Physique, tom. lii, p. 178.

the diminution of volume which atmospheric air sustained was 23, in a second 23.6, and in a third 26 *. There can be no doubt, therefore, of the immediate absorption of nitrogen by these liquids. There is reason to believe also, as has been already observed, that the condensed nitrogen enters slowly into combination with the hydrogen of the sulphuretted hydrogen, forming ammonia, and thus a fresh quantity will be successively absorbed. This explains the result in Scheele's experiments, that when atmospheric air was exposed to their action for two weeks, the diminution of volume amounted to 27 or 28 in 100.

To obviate the first of these sources of error, the liquor, if newly prepared, ought, before it is used, to be agitated for a short time with a quantity of atmospheric air, that it may imbibe as much nitrogen gas as it can receive ; and in operating with it, any error will be more completely avoided by not using too large a quantity of liquid, the due proportion not exceeding 4 or 5 to 1 of atmospheric air by measure. When the absorption of oxygen is accelerated by agitation, there can be no sensible error from the combination of the nitrogen with hydrogen, as this takes place slowly. The residual air has a slightly fœtid smell, which might be ascribed to sulphuretted hydrogen, the presence of which may be supposed a source of error ; but if present, it is in a quantity inappreciable, as by washing the air with water this odour is removed, without any diminution of volume. There is only one case in which the method cannot well be applied, that in which the air analysed has an intermixture of carburetted or oxycarburetted hydrogen, as these gases, Saussure and Berthollet have remarked, are absorbed by the sulphuretted liquors.

The individual compounds of this class will be noticed

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* Journal de Physique, tom. lx, p. 132.

under the different bases with which the super-sulphuretted hydrogen is combined

There is some reason to believe, that other compounds of sulphur and hydrogen exist. In passing the vapour of sulphur over ignited charcoal, the younger Berthollet observed, that besides a peculiar product, which it now appears is a carburetted sulphur, different liquids were produced, which appeared to contain sulphur and hydrogen, from some of which, by partial distillation, prismatic crystals were formed. And when the proportion of sulphur was large, a solid product was deposited, having a fœtid smell, and which when heated gave out sulphuretted hydrogen,—which appeared therefore to be concrete hydrogenated sulphur. But the composition of these products has not been particularly investigated.

CHAP. III.

OF CARBONIC ACID, ITS BASE, AND THEIR COMBINATIONS.

No discovery contributed more to the progress of Chemistry than that by Dr Black, of an aëriform fluid existing in combination with the alkalis and some of the earths, and capable of being disengaged from them, so as to be obtained in an insulated form. To this elastic fluid, the principal chemical agencies of which he ascertained, he gave the name of Fixed Air. Bewly and Bergman discovered that it is an acid; and from existing in the atmosphere, it received the name of Aërial Acid. It was also known to be produced in the combustion of charcoal; and

at the framing of the new nomenclature, the term Carbon being introduced to denote the pure inflammable matter of charcoal, this gas, the product of its oxygenation, was named Carbonic acid. Carbon exists in various states of combinations, forming several important compounds. Its purest form, perhaps, is the Diamond; for this valuable gem is not only an inflammable body, but, it has been demonstrated, affords, in burning, the same product as common charcoal. The mineral known by the name of Plumbago consists principally of carbonaceous matter. When charcoal receives a certain portion of oxygen, it is converted into an elastic fluid, which, having no acid properties, has been named Carbonic Oxide; and when fully oxygenated, it forms, as has just been remarked, Carbonic Acid. There exist, besides, several compound gases, of which carbon is the base, combined with hydrogen, and some of them also probably with oxygen, forming Carburetted and Oxycarburetted Hydrogen Gases. And it likewise forms a definite compound with sulphur, Carburetted Sulphur. The history of all these substances forms the subject of the present chapter. To the substance which is their common base, it is convenient to have a general name by which it can be designated; with this view the term Carbon has been introduced; and in diamond, and well calcined charcoal, it is probably not far from being in a pure state. It is a chemical principle of much importance, carbonaceous matter being the principal ingredient of all vegetable, and of many animal substances, besides being extensively distributed in the mineral kingdom. Diamond may first be considered as the purest form under which it occurs.

SECT. I.—*Of Diamond.*

THE Diamond has always been regarded as the most valuable of the gems, a superiority which it derives from its high lustre and hardness. The first quality arises from its great refractive power, which is such as to cause all the light to be reflected which falls on it at an angle of incidence greater than of 24½ degrees. From its hardness, its lustre remains uninjured: This hardness is such, that it can be cut, or rather worn down only by rubbing one diamond against another, and is polished only by the finer diamond powder. It occurs either in perfect crystals or fragments, is colourless or tinged of various shades, generally transparent, of a laminated structure, and having a specific gravity of from 3.5 to 3.6. It is found in India and in Brazil; and always in alluvial situations.

The diamond is phosphorescent. It becomes electrical on rubbing, the electricity being positive.

From the qualities of the diamond, it was ranked with the other gems, and considered as analogous to them in its chemical constitution. Newton, by a happy application of a physical principle, conjectured that it is an inflammable substance. Transparent bodies which are uninflammable refract light nearly in the ratio of their density, while those which are inflammable have refractive powers which are greater than their densities; and the diamond having this great refractive power, led Newton to conclude, that it " probably is an unctuous substance coagulated *." In 1695, experiments had been made at Florence, which proved the diamond to be dissipated by the intense heat in the focus of the powerful burning lens of Tschirnausen. Afterwards, in experiments made at

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* Optics, Book II, Prop. 10.

Vienna, it was found, that in the heat of a furnace, diamonds lost weight, and at length entirely disappeared, while the ruby and other gems exposed to the same heat. remained unaltered. At a latter period, D'Arcet exposed diamonds to heat inclosed in balls of porcelain clay, and found that they were dissipated by a strong heat These facts appeared in contradiction to the practice of the jewellers, who expose diamonds which are foul to a strong heat, imbedded in charcoal, to render them clear. An observation of Macquer first threw light on the subject. He took notice, that while the diamond was exposed to heat under a muffle, and while it was losing weight, it was luminous or appeared to burn, a fact which he verified by subsequent experiments. In the experiments of D'Arcet, therefore, air had been admitted to the diamonds from rents in the porcelain clay balls in which they were inclosed, while in the method of the jewellers, they are protected from the action of the air by the charcoal dust around them.

To remove the uncertainty attached to this subject, Lavoisier, with Macquer and Cadet, undertook some experiments. They ascertained, that in close vessels the diamond does not evaporate by exposure to heat; and repeating the experiment of the jewellers, they found that when imbedded in charcoal powder from which the air was excluded, the most violent heat produced no change. They were therefore disposed to conclude, that the dissipation of the diamond, when heated in the open air, is owing to its combustion[*]. Facts similar to these were established by a second series of experiments performed by D'Arcet and Rouelle. And Lavoisier, in another memoir, demonstrated more decisively the combustibility of the diamond, and discovered the product of its combustion. When suddenly heated by a lens, he found it to decrepitate; when heat-

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Mémoires de l'Acad. des Sciences, 1772, p. 350.

ed more slowly it was dissipated without decrepitation.
When heated by a lens in a glass vessel over water, it was
dissipated, and no sensible product was obtained ; in a se-
cond experiment, he observed, that when the heat was less
powerful, the surface of the diamond became black, and
was covered with a thin coating of charcoal.   In a subse-
quent experiment, he found, that the air was diminished
in volume, to the extent of about 8 cubic inches in 60 ; on
pouring into this residual air, lime·water, it became milky,
as it would have done from exposure to air in which char-
coal had burned; and by subjecting it to different trials,
this milkiness was found to be owing to the presence of
carbonic acid, which of course had been produced during
the combustion of the diamond.   Hence he drew the con-
clusion, that the diamond is a combustible body ; and that
there exists a great analogy between it and charcoal *.

Some years afterwards, Guyton shewed that the diamond
is consumed when heated with nitre, and affords carbonic
acid.   This experiment was repeated by Mr Tennant, by
exposing to a red heat, in a gold tube, two grains and a
half of diamond with a quarter of an ounce of nitrate of
potash.   The potash of the nitre retained the carbonic acid
formed : being dissolved in water a solution of muriate of
lime was added, by which carbonate of lime was formed,
and from this the carbonic acid was disengaged by mu-
riatic acid.   The quantity Mr Tennant found to be about
equal to what ought to have been obtained from two grains
and a half of charcoal combined with oxygen ; and he there-
fore concluded that the diamond is charcoal, and differs
from that substance only in its state of aggregation and its
crystallized form †.

Guyton, again, undertook the investigation of this sub-
ject, exposing a diamond to the rays of the sun, concentrat-

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* Mémoires de l'Acad. des Sciences, 1772, p. 500.
† Philosophical Transactions, 1797, p. 123.

ed by a powerful lens, in a vessel of oxygen gas. It was
soon sensibly blackened on its surface; the appearance of
combustion then became evident; an instant after it be-
came brilliant, and at some points it appeared to boil; it
gradually diminished and the application of the solar heat
was repeated, until it was entirely consumed. The quan-
tity of carbonic acid produced was ascertained by intro-
ducing a solution of barytes in water, and the unexpected
result obtained, that the quantity was greater than what
would have been formed by the combustion of the same
weight of charcoal as of diamond. Twenty-eight parts of
charcoal in burning combine with 72 of oxygen, and form
100 of carbonic acid; while the same weight of acid, ac-
cording to Guyton's experiment, is formed from the com-
bustion of 17.88 of diamond, which thus combine with
82.12 of oxygen. Guyton concluded, therefore, that the
difference between diamond and charcoal does not depend
on the state of aggregation, nor are the distinctive pro-
perties of charcoal owing to the small residue which it leaves,
or to the minute quantity of hydrogen which it may con-
tain, but to its oxidation, diamond being the simple base
of which charcoal is an oxide.

The experiments of Guyton were not, however, satis-
factory, particularly as to the estimation of the quantity of
carbonic acid. Berthollet has, in particular, pointed out
the source of error in the assumption, that the carbonate of
barytes formed, by introducing barytic water to the gas
after the combustion, contained the same proportion of
carbonic acid as that in the native carbonate [*].

Messrs Allen and Pepys, from the consideration of the
uncertainty of these results, undertook a series of experi-
ments with the view of determining the question [†]. They

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[*] Mémoires de l'Institut National, t. iv, p. 288.
[†] Philosophical Transactions, 1807.

employed a tube of platina, placed across a furnace, and connected at each extremity with a mercurial gazometer; a small platina tray was placed within the tube, containing the diamond operated on; and the tube being at ignition, oxygen gas, the purity of which had been ascertained, was passed slowly through it, from one gazometer to the other, and was thus made to pass over the diamond a number of times. At the end of the experiment, the whole of the gas being collected in one gazometer, the quantity of carbonic acid produced was estimated from the volume of it absorbed by lime-water; the quantity of oxygen which had been consumed was discovered; and the quantity of the diamond consumed was ascertained. The composition of the carbonic acid could thus be inferred, either from the consumption of a given weight of oxygen, or of carbonaceous matter. The results by each mode differed little; and in two experiments it was found, estimating from the quantity of oxygen consumed, that 100 parts of carbonic acid contain, according to the one, 28.81 of diamond; according to the other, 28.72. The proportions from charcoal and oxygen are almost precisely the same, the quantity existing in 100 parts of carbonic acid estimated from the same mode being 28.77. It may therefore be concluded, that diamond and charcoal are essentially the same, and differ only in their aggregation and form.

Biot had supposed, that the diamond, from its high refractive power, must contain hydrogen in a considerable proportion. Guyton executed a series of experiments, with an apparatus similar to that of Messrs Allen and Pepys, to determine this. The results were altogether incompatible with Biot's opinion. He seemed disposed to conclude, in conformity to his former opinion, that while the diamond is the pure inflammable base, charcoal might contain oxygen, though in small proportion; but in sup-

port of this, his own experiments afforded no sufficient evidence *.

Mr Davy supposed, that the diamond may contain a small portion of oxygen, chiefly from some results obtained in heating it with potassium. It became of a gray colour, and the product when acted on by water produced one cubic inch and $\frac{3}{15}$ of hydrogen, while the same quantity of potassium as that which had been employed, exposed to a similar heat, evolved in its action on water one cubic inch and $\frac{7}{10}$ of the same gas †. From an experiment on quantities so minute, and affording a difference so inconsiderable, it is obvious that no conclusion can be drawn.

In subsequent experiments on the combustion of the diamond, excited by the concentrated solar rays in dry and pure oxygen gas, Sir H. Davy found, that not the slightest trace of vapour or humidity appeared; the interior of the glass vessel appeared as clear as before the experiment; pure carbonic acid gas was the sole product, and was formed from the oxygen gas without any change of volume. In executing similar experiments on plumbago, and on charcoal which had been strongly ignited, the gas, during the combustion, became clouded, and moisture was deposited, with a sensible diminution of volume. The diamond, when heated intensely in chlorine gas, which, by forming muriatic acid with hydrogen, gives indication of that element, suffered no change, while plumbago and charcoal, submitted to the same experiment, immediately afforded this proof of its presence. These results seem to prove, that diamond is pure carbon, and that the other carbonaceous substances contain a minute portion of hydrogen. The quantity of this, however, is so small, as scarcely to admit the conclusion, that the difference of properties de-

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* Annales de Chimie, t. lxxxiv; t. lxxxvi.
† Philosophical Transactions, 1809.

pends on it; it is doubtful even if it is not altogether ad-
ventitious; and the conclusion is still most probable, that
the peculiar characters of the diamond arise from its state
of aggregation and crystalline form *.

A striking fact with regard to the oxygenation of the
diamond, is the high temperature which is requisite to it
taking place. It appears, from Guyton's statement, to be
charred at a heat of 18 or 20 of Wedgwood's scale (3417
or 3677 of Fahrenheit's), and at about 30 (4977°) it burns
with a feeble flame, nor does it even in oxygen gas pro-
duce so much heat as to support its combustion. This is
no doubt owing to the strong cohesion exerted between its
particles †. Sir H. Davy has found, however, that when
the diamond is exposed in a capsula of platina, perforated
so as to be exposed to a free circulation of the gas, it con-
tinues to burn when withdrawn from the focus of the lens,
and that it produces intense heat.

The appearances attending the combustion of diamond
were observed with accuracy by Sir George Mackenzie,
and the temperature requisite found to be less high;
indeed the temperature assigned by Guyton was rather
from conjecture than from experiment. A diamond cut
and polished, when introduced into a muffle heated red
hot, soon acquired the same redness as the muffle, but in
a few minutes more became distinguished by a bright glow,
and began to consume. A piece of plumbago placed be-
side it exhibited a similar luminous appearance at a lower
temperature. When the air was excluded from the muffle,
both lost their brightness, but it returned on the admission
of the air, and was increased by blowing on them with bel-
lows. The temperature at which the combustion of the
diamond takes place was indicated by the pyrometer of

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* Philosophical Transactions, 1814.

† Memoir by Guyton, Annales de Chimie, t. xxxi.; or Ab-
stract of it in Nicholson's Journal, 4to, vol. iii, p. 298.

Wedgwood to be about 14 or 15 of the scale. Though the temperature, therefore, is lower than that which Guyton had assigned, it is still much higher than that necessary for the combustion of charcoal.

Sir George Mackenzie confirmed an experiment of the French Chemists, in which soft iron was converted into steel by being heated with diamond; and his experiments are more satisfactory, as having been made with diamond in its purest state *.

The diamond is scarcely acted on by any other agent than by oxygen at an elevated temperature. Bergman states an experiment from which it would appear to be partially oxidated by sulphuric acid; this acid, when poured on the diamond powder, previously freed from impurities by digestion with nitro-muriatic acid, and evaporated to a small quantity, becoming black, and depositing small pellicles, which take fire on the approach of flame, and are consumed. The other acids, according to his observation, exert no sensible action on it; nor does it appear, from the experiments which he made on it with soda, (the mixture of soda and of diamond powder being exposed to a very strong heat,) that it had suffered any chemical change from the action of the alkali; for although a minute portion of earthy matter seemed to be produced, this might probably be derived from the various agents employed in the experiment †.

SECT. II.—*Of Plumbago.*

PLUMBAGO.—This substance, known in commerce by the name of black lead, the Plumbago and Graphite of Miner-

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* Nicholson's Journal, 4to, vol. iv, p. 103.
† Essays, vol. ii, p. 118.

alogists, is a mineral production, the nature of which was not understood until in some measure pointed out by Scheele. He shewed that, by slow combustion, or by heating it with nitre, it is converted into carbonic acid with a small residuum of iron *. Experiments were afterwards made upon it by Pelletier, by Monge, and Vauquelin, whence it appeared to be a compound of carbon with iron, containing from 5 to 10 parts of iron in 100. Scheele observed that it required more nitre to burn it than charcoal ; but this was supposed to be owing to its difficult combustibility, in consequence of its aggregation and its combination with the iron, from which much of the oxygen of the nitre was dissipated without being spent in the combustion. Guyton supposed, however, that it requires more oxygen for its saturation than charcoal does, and that a given weight of it produces a larger quantity of carbonic acid ; and hence he concluded, that it approaches nearer to the simple base, or might be regarded as carbon in the first degree of oxidation.

This conclusion was not established by any decisive evidence ; and by the experiments of Allen and Pepys, it is proved to be incorrect. They submitted pure plumbago to the experiment already described under the history of diamond ; it was consumed leaving only a very small residuum of iron. Estimating from the quantity of it consumed, and the quantity of carbonic acid formed, it was found, that 100 parts of the acid contain 28.66 of the carbonaceous matter of plumbago ; and the same proportions were found from the quantity of oxygen that had disappeared. The carbonaceous matter existing in plumbago, it may be inferred, therefore, from these experiments, is nearly the same as that composing diamond. The experiments of Sir H. Davy, already stated, seem to shew that it contains a minute portion of hydrogen ; but the quan-

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* Chemical Essays, p. 243.

tity is extremely inconsiderable, and when it is submitted to the action of voltaic electricity, it gives no traces of hydrogen.

The carbonaceous matter in plumbago is combined with iron, which is variable in quantity, but a certain portion is always present, and hence perhaps it may be considered as an essential ingredient. It is therefore to be afterwards noticed as a carburet of iron. Its carbonaceous matter approaches so far in chemical properties to diamond, as not to burn except at a very elevated temperature, and not to evolve so much heat as is requisite to keep up its combustion, probably from its state of aggregation, or partly from its combination with the iron. It is also perfectly infusible.

Th. Saussure has stated, that 100 parts of plumbago contain 4 of iron; and that 100 parts of carbonic acid, formed from its oxygenation, contain between 27.04 and 27.38 of its carbonaceous matter.

Another substance into which plumbago graduates, is that named Mineral Carbon, Anthracite, or Glance Coal. It is of a black colour, with some lustre, is soft, smooth and light. When exposed to heat, it does not, like the other coals, exhale any bituminous or sulphureous vapour. It burns very slowly, with a red glow, but without flame. The greater part of it consists of carbonaceous matter, with portions of silica, alumina, and oxide of iron. Guyton considered its carbonaceous matter as in an imperfect state of oxidation approaching to plumbago; and with regard to one variety of it, the blind Kilkenny coal, he remarks from Kirwan, that it is capable at ignition of decomposing nearly as much nitre as plumbago does. The carbonaceous residuum, which is obtained from the decomposition of animal substances by heat in close vessels, is scarcely capable of combining with oxygen but at a high temperature; and even coal, when it has been coaked or exposed to a strong heat in close vessels, is not so easily

kindled as common wood charcoal. Messrs Allen and
Pepys found that they are all essentially the same with
charcoal. The anthracite, when submitted to experiment,
consumed the same quantity of oxygen, and afforded the
same quantity of carbonic acid, 100 grains of carbonic
acid containing 28.27 of its combustible matter. Animal
charcoal contains hydrogen with a little saline matter;
and, according to Doebereiner, retains a portion of nitro-
gen.

Sect. III.—*Of Charcoal.*

WHEN vegetable matter, especially that which forms the
solid parts of plants, is exposed to heat in close vessels, it
is decomposed ; the more volatile principles are disenga-
ged, and there remains a black shining porous substance,
composed of the matter not convertible to the gaseous form.
This is CHARCOAL. It is usually obtained from the im-
perfect combustion of wood. The wood cut into billets,
or the branches of trees from which the smaller twigs have
been lopt off, being heaped together in a pyramidal pile,
which is covered with earth or turf, in which a few aper-
tures are left, heat is applied so as to kindle the internal
parts of the pile. The apertures are nearly closed, that
the combustion may be carried on slowly, and in an im-
perfect manner ; the moisture of the wood is dissipated ;
its more volatile principles, particularly its hydrogen and
oxygen, pass off in combination with part of its carbon ;
and the residual mass, consisting principally of carbon, is
the black porous substance, common charcoal. It gene-
rally retains the figure and texture of the wood from which
it has been prepared, and is obtained in largest quantity
from the more dense and hard woods. This is the pro-
cess which is carried on, on a large scale, to obtain char-

coal. It is obtained in a more perfect state of preparation by exposing pieces of wood in an iron retort, or covered with sand in a crucible, to a very strong fire for an hour or two; the high temperature thus excited producing a more complete decomposition of the ligneous matter than the imperfect combustion in the other mode.

It is evident, that the residual charcoal in these processes must contain any other fixed principle which may have existed in the wood. It accordingly always contains a portion of saline and earthy matter, chiefly carbonates of potash and lime, and a little oxide of iron, which remain when it is burnt; but the quantity of these is very inconsiderable, seldom amounting to a 200dth part. Other processes have been given to obtain charcoal. Fixed oil, in burning, deposites a quantity of black powder, which when it has been exposed to a red heat, without the access of air, has been supposed to afford nearly a pure charcoal: it always contains, however, a little saline matter. A similar product is obtained, by passing oil or ardent spirit through an ignited tube.

Lavoisier regarded charcoal, apart from the small quantity of earthy and metallic matter contained in it, as pure carbon; and the experiments of Tennant, already stated, appeared to prove its identity with diamond. Guyton inferred, from his experiments which have been already stated, that it is an oxide of carbon: 18 of diamond affording 100 of carbonic acid in burning, while 28 of charcoal are necessary to form the same quantity, the difference, or 10, is the quantity of oxygen which 28 of charcoal contain; and in 100 parts, therefore, it must consist of 64 carbon and 36 oxygen.

The experiments of Allen and Pepys have shewn the inaccuracy of Guyton's conclusions. With the apparatus already described, they burnt charcoal by transmitting over it oxygen gas; the charcoal having been exposed to a red heat immediately before submitting it to experi-

ment, and being weighed as speedily as possible, indeed
while still warm, so as to guard against any fallacy which
might arise from its hygrometric quality, in consequence
of which it absorbs humidity from the atmosphere.   The
charcoal was almost entirely consumed, 4 grains leaving
a white matter weighing only 0.02 of a grain.   Calcula-
ting from the quantity of charcoal consumed, and the
quantity of carbonic acid produced, it followed, that 100
grains of carbonic acid contain 28.92 of charcoal.   This
was confirmed by making the estimate also from the quan-
tity of oxygen consumed, the result from this being, that
in 100 grains of carbonic acid 28.77 of charcoal are con-
tained, both agreeing almost precisely with the results
from the combustion of diamond *.   From these facts the
conclusion seems to follow, that the inflammable matter
of charcoal is pure carbon, the same as the diamond,
and that the proportions of the elements of carbonic acid,
72 of oxygen and 28 of carbonaceous base, assigned by
Lavoisier, are nearly just.

There are some facts, however, from which it has
been inferred, that charcoal contains hydrogen.   When it
is exposed in close vessels to a strong heat, a large quan-
tity of an inflammable gas is procured from it, which on
burning affords water ; and when charcoal is burnt in
oxygen gas, a little water is condensed on the sides of the
receiver.

These facts may be explained, however, from the ope-
ration of the quantity of water which charcoal absorbs by
hygrometric affinity from the air.   Of this absorption
there is sufficient proof; charcoal after ignition increasing
in weight on exposure to the air, and affording after this
exposure water when urged by heat, as Allen and Pepys
have shewn.   To obviate this source of fallacy, and to
prove that charcoal, even when calcined, contains hydro-

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gen, Berthollet adduced some other results apparently
more conclusive.

Cruickshank had found, that when dry charcoal, which
had been obtained by distillation in iron cylinders, was
exposed to heat, a large quantity of gas was expelled from
it, inflammable, and which, except at the very commence-
ment, scarcely contained a vestige of carbonic acid; but
had the hydrogen of this elastic fluid been derived from
humidity in the charcoal, it ought, as he contended, to
have contained a large proportion of carbonic acid, form-
ed by the combination of the oxygen of the water with
the charcoal *.   Berthollet had also, at an early period,
observed the production of carburetted hydrogen with lit-
tle carbonic acid, from exposing charcoal to heat.   He
farther remarked, that in Lavoisier's experiment of burn-
ing charcoal in oxygen gas, to ascertain the nature of the
product, there was not only a deposition of water when
common charcoal was employed, but even when the char-
coal was well calcined, a quantity of water appeared on
the sides of the vessel at the commencement of the expe-
riment, which was afterwards dissolved by the carbonic
acid gas †.   And he adds an experiment by Hassenfratz,
which he had repeated with success, that of passing oxy-
gen gas through an ignited tube containing well calcined
charcoal; at the beginning of the operation, water is de-
posited at the end of the tube, and the gas deposites water
on cooling ‡   Another proof of the existence of hydrogen
in charcoal is derived from an experiment by Kirwan;—
exposing to heat " a mixture of equal parts of sulphur
" and pulverized charcoal, out of which its adventitious
" air had been as much as possible expelled by keeping

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* Nicholson's Journal, 4to, vol. v, p. 210.
† Mémoires de l'Institut National, tom. iv. p. 287.
‡ Ibid. p. 326.

" it a long time heated to redness :" sulphuretted hydro-
gen was procured in large quantity [*].

From these facts Berthollet drew the conclusion, that
" Charcoal is a combination of carbon and hydrogen, with
" a small quantity of oxygen; it loses by the action of
" heat the oxygen, and a certain proportion of the hydro-
" gen and carbon : after this calcination, it ought to be con-
" sidered as a combination of carbon, and of a small pro-
" portion of hydrogen [†]." The diamond he regarded as
pure carbon ; and he supposed that it is owing to this ab-
sence of hydrogen that it is less combustible than charcoal,
or requires a more elevated temperature to burn.

Clement and Desormes maintained the opposite opi-
nion, that no sensible proportion of hydrogen is contain-
ed in well calcined charcoal [‡]. They observe, that al-
though in its usual state of preparation, it gives out in-
flammable gas by exposure to heat ; this diminishes, and
at length ceases, even though the heat be raised to the
utmost intensity ; and after this there is no proof that it
contains hydrogen. They farther found, by experiment,
that when well calcined charcoal is removed from a fur-
nace, and placed in an apparatus, in which, without pre-
vious exposure to the air, it can be made to burn, no sen-
sible portion of water is produced ; muriate of lime, a salt
strongly attractive of moisture, gaining no weight when ex-
posed to the gas formed by its combustion, or, at farthest,
gaining so much as not to give a quantity of hydrogen in
charcoal more than $\frac{1}{1500}$, that is, a quantity scarcely ap-
preciable. They found also, that the quantities of carbo-
nic acid produced in the combustion of different varieties
of charcoal, plumbago and anthracite, are from equal
weights the same, and that these substances in burning re-

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[*] Philosophical Transactions, vol. lxxvi, p. 124.
[†] Mémoires de l'Institut National, tom. iv, p. 315.
[‡] Philosophical Magazine, vol. xiii, p. 67, 158.

quire nearly the same quantity of oxygen. Several of these facts were confirmed by Allen and Pepys. They observed, in particular, that in burning charcoal, by supplying it, when ignited, with a stream of oxygen gas, there is no appearance of moisture. The production of sulphuretted hydrogen, from the mutual action of sulphur and charcoal at a red heat, is not established. If any is produced, it is owing to the charcoal not having been thoroughly calcined. If this has been done, Clement and Desormes affirm, that though a little gas is obtained, it is not sulphuretted hydrogen, and the liquid which is the principal product is not, as had been supposed, a compound of sulphur and hydrogen, but, as is to be afterwards stated, a compound of sulphur and charcoal.

There is one chemical agent by which the presence of hydrogen in charcoal is discovered with great minuteness of effect,—chlorine or oxymuriatic gas. It is converted by the action of hydrogen into muriatic acid; and accordingly, when this gas is transmitted over ignited charcoal, which has been previously calcined even at a very intense heat, muriatic acid gas is formed. The effect, however, at length ceases, and the charcoal remains without any apparent alteration in its properties.

The action of voltaic electricity in high intensity on thoroughly calcined charcoal, gives results favourable to the conclusion, that it contains a minute quantity of hydrogen. Davy found, that in exposing it to the action of the galvanic battery, in the Torricellian vacuum, brilliant light and flame of a purple colour were produced ; a small quantity of aërial fluid was given out, amounting to nearly an eighth of a cubic inch from half a grain of charcoal, which was inflammable. The charcoal had become harder at the point, and its lustre, where it had been heated to whiteness, approached to that of plumbago. In heating charcoal with potassium, there was no ignition, and no production of elastic fluid ; nor was there any proof

of oxygen being afforded to the potassium in the process ;
for the compound acted on water with energy, and pro-
duced a quantity of inflammable gas only inferior by one-
twelfth to that produced by pure potassium, and which
gave the same diminution by detonation with oxygen ; the
slight difference in quantity might therefore be ascribed
to the influence of foreign matter in the charcoal. This
appears to prove, that charcoal contains no oxygen.

The general result on this subject seems to be, that char-
coal, in its common state of preparation, contains a portion
of hydrogen, part of that element existing in those sub-
stances from which charcoal is formed, and retained by its
affinity to the carbonaceous base. The inflammable elas-
tic fluid, which is first given out when charcoal is heated,
may be derived partly from the water absorbed from the
atmosphere; and accordingly, it appears to contain not only
hydrogen combined with carbon, but also oxygen in the
state of carbonic acid, carbonic oxide, or oxycarburetted
hydrogen. As the heat is raised, the gas approaches nearer
to that of pure hydrogen combined with carbon, and the
quantity of it diminishes. At length its production ceases.
But even when the most intense heat has been applied, a
minute portion seems to remain, which appears in the pro-
duction of water, when this calcined charcoal is acted on
by oxygen, or of muriatic acid when it is submitted to the
action of chlorine. The quantity, however, is extremely
inconsiderable; in some cases less, according to Sir H.
Davy's estimate from his experiments, than $\frac{1}{50000}$. The
question is, is this essential to charcoal ? There is a diffi-
culty with regard to either conclusion. If it is not retain-
ed by a very powerful attraction, how is it not expelled by
a heat so intense ? If it is retained in combination, it must,
in conformity to the usual law, be supposed to exist in a
definite proportion ; yet the quantity is so small that it can
scarcely be brought under the law of multiples, in relation

to the other definite proportions, in which hydrogen enters into chemical combination. And although there is reason to believe that hydrogen exists in lower definite proportions than in any of the binary compounds, from which its combining weight has been inferred, yet still the difficulty remains to a considerable extent. It appears too, that this minute portion of hydrogen does not modify the properties of charcoal; for when all effect ceases to be produced by the action of chlorine, the appearance and properties of the charcoal remain the same. Hydrogen, therefore, can scarcely be considered as essential to its chemical constitution.

Wood-charcoal, in its usual state of preparation, is a solid, porous substance, of a deep black colour; tasteless and inodorous. When obtained from the decomposition or imperfect combustion of some vegetable substances it is in the state of a black spongy powder.

Charcoal is altogether infusible by heat; nor in close vessels is its texture, or any of its physical properties changed, though it is urged by the most intense fire It remains unmelted, and has been even dissipated in vapour by the intense heat of a very powerful galvanic battery, without any sign of previous fusion : it has thus been rendered so hard as to scratch glass. Under some circumstances, its surface exhibits a degree of metallic lustre.

When heat is first applied to charcoal, so as to bring it to ignition, a quantity of gas is disengaged, and the production of this continues for some time. It consists of carbonic acid, and of a variety of carburetted hydrogen, which vary considerably in their relative proportions from different varieties of charcoal; the first however is always in much smaller proportion ; it diminishes as the experiment proceeds , and towards the end it is scarcely in any appreciable quantity. The inflammable gas is in large quantity. Berthollet obtained 720 cubic inches from one ounce

of charcoal *; and the charcoal lost nearly one-fourth of its weight. Clement and Desormes found, that when common charcoal was exposed to a strong heat, in an earthen retort, or iron tube, for two hours, it gave out gas only the first hour; during the second it yielded none †. This production of an aëriform fluid by heat from common charcoal, is probably in part owing to the decomposition of the water it contains,—the elements of which enter chiefly into a ternary combination with part of its carbon, and form the inflammable gas; and partly to portions of the hydrogen and oxygen of the vegetable matter remaining in the charcoal, prepared in the usual mode, and being disengaged in combination with carbon at a high temperature. It does not appear, that by this process the physical or chemical properties of the charcoal are materially changed. It is rendered a better conductor of galvanism.

Charcoal is altogether insoluble in water; nor at a moderate temperature is it in any way affected by it. Wood, therefore, which has been charred, is preserved a long time unchanged, though exposed to humidity, or immersed in water; and solid vegetable matter, which, under exposure to water, has suffered spontaneous decomposition, is converted into a black substance, consisting principally of charcoal, beyond which the decomposition does not proceed. Charcoal when newly calcined absorbs humidity from the atmosphere quickly, and to such an extent as to be sensibly increased in weight. According to Clement and Desormes, a piece of charcoal weighing 4 grammes (61.7 grains,) on exposure to a dry atmosphere, increased in weight 0 2 of a gramme (3 grains) ‡. Messrs Allen and Pepys found, that different kinds of charcoal increased in weight from a week's exposure, after they had been thoroughly ignited,

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* Mémoires de l'Acad. des Sciences, 1781, p. 228.
† Annales de Chimie, t. xxxix, p. 29.
‡ Ibid. tom. xlii, p. 123.

from 10 to 18 *per cent.*; and as they increased little in weight in confined air, the increase must be ascribed to absorption of water from the air. They also found, that the greatest increase took place in the first hour or two after exposure, and arrived at its maximum in 24 hours. This absorption appears to be hygrometric, and is not produced by any other substance to the same extent. By exposure to heat, this water is expelled, partly undecomposed, and partly in new combinations of its elements with the charcoal. At ignition water is decomposed by charcoal, and carbonic acid and an inflammable gas a compound of carbon and hydrogen are formed.

A singular property of which charcoal is possessed is that of absorbing aëriform fluids, and condensing them in its pores, without forming with them any intimate chemical combination, or suffering any change in its properties. The effect is exhibited, by removing a piece of charcoal, when red-hot, into a tube filled with quicksilver; if when it has cooled in this situation, a quantity of aëriform fluid be admitted into the tube, an absorption takes place many times the bulk of the charcoal.

This property had been made the subject of experiment by Scheele, Priestley, and Fontana; and was examined with more attention by Morozzo and Rouppe. Morozzo employed pieces of charcoal of a determinate size (1 inch in length, and 8 lines in diameter,) which, after being ignited, he plunged into mercury, and introduced into a glass tube, of an inch in diameter, and 12 inches long, placed in the mercury, and filled with the gas designed to be submitted to trial. The following table shews the proportions of the gases that were absorbed.

	Inches.	Lines.
Atmospheric air,	3	6
Carbonic acid gas,	11	
Nitric oxide gas,	6	10
Hydrogen gas,	2	1

	Inches.	Lines.
Oxygen gas, ...	2	2
Ammonia, ...	11	
Muriatic acid gas, ...	11	
Sulphuretted hydrogen gas, ...	11	
Sulphurous acid gas, ...	5	6 *

These experiments were repeated and varied by Rouppe and Van Noorden. They employed an apparatus, in which the charcoal, in a state of ignition, was allowed to cool without exposure to the air, and without being plunged in quicksilver ; and, when cold, the air was exposed to it, the absorption being indicated by the rise of the water, in which the tube containing the air stood, and by which the pressure of the atmosphere was less counteracted than in the experiments where quicksilver was employed. The pieces of charcoal were about 16 or 17 inches in volume. The quantities of the airs absorbed were in the following proportions :

Atmospheric air, 36 inches immediately, and in 4 or 5 hours, 48.

Oxygen gas, 30 inches immediately, and slowly to 46.

Nitrogen gas, 27 inches immediately.

Nitric oxide gas, slowly to the extent of 136 inches.

Hydrogen gas, from 29 to 31 inches immediately.

Carbonic acid gas, 230 inches immediately †.

Morozzo resumed his experiments, with an apparatus in which the charcoal was exposed to the gases without having been immersed in quicksilver, being introduced into a closed cavity, which communicated by a stop-cock with a glass tube containing the gas to be submitted to experiment. The results differ from the former with regard to some of the gases, and agree as to others. Atmospheric air suffered a diminution of volume of about one-third, instead of only about one-fourth as before. Oxygen pre-

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* Journal de Physique, 1783.

† Annales de Chimie, tom. xxxii, p. 1.

sented a deviation still more striking; the absorption, instead of being only 2 inches out of 12, amounting to 12 out of 18, in 4 hours; in 48 hours to 13 inches 6 lines; in 3 days, 14 inches 5 lines; and in 8 days being total. The absorption of hydrogen and of carbonic acid gases appeared to be the same in the second as in the first experiments. That of nitrogen gas was found to amount to 6 inches in a tube 18 inches long; on referring to the standard in the above table, it would be equal to 4 *. These experiments appear to have been made on the charcoal before it had cooled much, in which respect they differ from those of Rouppe, and are less accurate, as at a high temperature chemical action may take place.

T. Saussure has since instituted similar experiments, employing the charcoal of boxwood, which does not sensibly absorb quicksilver, introducing it into the quicksilver while red hot, and then allowing it to rise to the surface when it had cooled, so as to be exposed to the gas in a tube. The following table gives the quantities absorbed at the end of 24 or 36 hours, when the absorption had in general ceased.

Ammoniacal gas, ... 90 volumes.
Muriatic acid, ... 85
Sulphurous acid, ... 65
Sulphuretted hydrogen, ... 55
Nitrous oxide, ... 40
Carbonic acid, ... 35
Olefiant gas, ... 35
Carbonic oxide, ... 9.42
Oxygen, ... 9.25
Nitrogen, ... 7.5
Oxycarburetted hydrogen, ... 5
Hydrogen, ... 1.75
An elevation of temperature was produced in all these

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* Nicholson's Journal, vol. ix, p. 255; vol. x, p. 12.

cases, greater in general as the absorption was more ra-
pid *.

Several interesting facts have been ascertained with re-
gard to this condensation of airs by charcoal, by Rouppe.
It had been supposed that they suffer some changes be-
sides condensation ; but according to his experiments they
do not ; and when they have appeared to do so, he supposes
it owing to the charcoal having been previously exposed to
another gas, or to atmospheric air, or sometimes to incan-
descent charcoal having been employed.   Sennebier stated
some experiments in which atmospheric air appeared to be
decomposed in this absorption, its oxygen being absorbed in
larger proportion than the nitrogen † ; but according to
Rouppe, atmospheric air is absorbed unaltered.   The great-
er part of the absorbed gas is again expelled by a heat in-
ferior to that of boiling water, and likewise to a certain ex-
tent by immersion in water.   Neither does the charcoal ap-
pear to be materially changed in its properties, and by ex-
posing it again to heat it can be employed with the same
effect in the experiment.   The pieces of charcoal, Morozzo
found increased a little in weight, generally from half a
grain to two grains.   Cold favours the absorption, evi-
dently by diminishing the elasticity of the gas.

Few phenomena can be regarded as more singular than
this absorption.   A large quantity of elastic fluid is con-
densed by the charcoal ; there must therefore have been
exerted a powerful attraction, by which the elasticity of
the gas has been overcome.   Yet this attraction can scarce-
ly be denominated chemical, since the gas appears to ex-
ist merely condensed in the pores of the charcoal, its pro-
perties, as well as those of the charcoal, remaining un-
changed ; gases too are thus condensed, to which char-
coal is not known to exert any chemical attraction, and

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* Annals of Philosophy, vol. vi, p. 242.
† Annales de Chimie, tom. iv. p. 261.

they are reproduced by a slight elevation of temperature. It is evidently connected with the porosity of the charcoal, and hence it is not exerted by charcoal powder.

Elastic fluids being thus condensed in the charcoal, it was supposed by Rouppe, that two gases having a mutual attraction might be brought into combination by this arrangement. He accordingly stated, that charcoal, which had been previously exposed to hydrogen gas, on being exposed to atmospheric air, did not absorb it unchanged, as pure charcoal would have done, but absorbed chiefly its oxygen, and a few drops of water appeared. Exposed to pure oxygen, the absorption was more rapid and considerable; and, by applying a thermometer to the charcoal, it was raised during the experiment from 52° to 100°. Charcoal, charged in like manner with hydrogen, absorbed and decomposed nitric oxide gas, water being formed and nitrogen gas being the residuum; charged with oxygen and exposed to hydrogen, there was also a formation of watery vapour: or, placed in nitric oxide gas, it caused a rapid and considerable absorption; charged with nitrogen, and exposed to atmospheric air, it is said to have deprived it almost entirely of its oxygen [*]. Saussure, however, was unable to obtain any of these results; and, as he justly observes, the quantity of hydrogen which could be absorbed is so small, that no appearance of water could be obtained.

As charcoal absorbs these aëriform fluids, so they at common temperatures appear to be capable of dissolving a small portion of it. Oxygen gas, when in contact with humid vegetable matter, abstracts carbon from it, forming carbonic acid; and from Saussure's experiments, it appears that the oxygen gas absorbed by charcoal is slowly converted into carbonic acid. From the experiments of Huber on Germination, it appears that hydrogen gas ex-

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[*] Annales de Chimie, tom. xxxii, p. 16.

posed to seeds moistened becomes impregnated with car-
bon.

At an elevated temperature charcoal enters into combi-
nation with oxygen, the combination being attended with
combustion.   Charcoal ignited burns in atmospheric air
without flame, but with a red glow, and the emission of
much heat : the compound it forms being gaseous, it ap-
pears to be entirely consumed, the residual ashes not a-
mounting to a 200dth part of the charcoal.   In oxygen
gas its combustion is more vivid, a white light with scin-
tillations accompanying it.   The product of the combus-
tion of charcoal is, as has been already stated, carbonic
acid.

In consequence of its affinity to oxygen, charcoal ab-
stracts that principle, both in the humid way and by the
application of heat, from many of its combinations, espe-
cially from water, the acids, and the metallic oxides and
salts.

Charcoal at an elevated temperature is capable of com-
bining with hydrogen.   This combination was obtained
by Priestley, by concentrating the solar rays by a lens on
charcoal placed in a vessel of hydrogen gas.   The com-
pound remains in the elastic form, with an increased spe-
cific gravity.   The same compound was obtained by Cle-
ment and Desormes, by passing hydrogen gas repeatedly
through an ignited tube containing charcoal.

With nitrogen, charcoal does not directly combine :
the experiments of Berthollet, however, prove that nitro-
gen is contained in ignited charcoal, and adheres to it
with much force, the last portion of elastic fluid expelled
from charcoal by an intense heat containing nitrogen gas[*].
And, according to Doebereiner, animal charcoal retains
nitrogen, which is discovered by heating it with oxide of
copper, carbonic acid gas, and nitrogen gas, being the

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* Mémoires d'Arcueil, tom. ii, p. 80, 484.

products in the proportion of 85 of the former to 15 of
the latter by volume . Gay-Lussac, too, as is to be after-
wards stated, discovered that a compound of carbon and
nitrogen is the radical of prussic acid, and that it can be
obtained insulated in the gaseous form. This substance,
therefore, Cyanogen, as he named it, is a carburet of ni-
trogen. In its decomposition, too, by heat, it leaves char-
coal, which retains a smaller proportion of nitrogen.

Charcoal combines with sulphur, forming a product,
carburetted sulphur, to be afterwards described.

Charcoal combines with several of the metals. These
combinations are to be afterwards noticed.

The action of the fixed alkalis on charcoal is doubtful.
If exposed to heat, mixed with soda or potash, a sub-
stance is obtained, which, when dissolved in water, gives a
liquor of a dark brown colour, which passes through the
filter ; and by boiling a solution of potash on charcoal
powder, a similar liquor is formed. Yet this has been
supposed to arise from the impurities, or the portion of
hydrogen present in charcoal not thoroughly calcined,
though perhaps without sufficient reason. Mrs Fulhame
found this solution to have the effect of charcoal in redu-
cing metallic solutions †.

A number of the acids are decomposed by charcoal,
their oxygen being attracted by it. Nitric, or nitrous
acid, suffers this decomposition from charcoal powder with
rapidity, its oxygen being abstracted, and nitrogen, nitric
oxide, and carbonic acid gases being di-engaged: if the
acid be concentrated, and the charcoal perfectly dry, and
somewhat warm, the oxygenation is so rapid as to be at-
tended with combustion. Sulphuric and phosphoric acids
are de-oxidated by its action.

A singular property possessed by charcoal, and depend-

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* Annales de Chimie et Physique, t. iii, p. 218.
† Essay on Combustion, p. 126.

ing on chemical agency, remains to be mentioned,—that of removing the taste, odour, and colour of vegetable and animal substances, especially those of a mucilaginous, oily or extractive nature. For the first accurate experiments of this kind, we are indebted to Lowitz of Petersburgh. They are extremely numerous; a few of the principal facts, therefore, only can be stated.

Common vinegar on being boiled with charcoal powder becomes limpid. Acid of tartar, when of a brown colour, is rendered colourless by its solution in water being boiled in the same manner; as are also solutions of crude tartar, crude nitre, and other salts, which, in their usual state of preparation, are of a yellow or brownish tinge, so that crystals are afterwards obtained perfectly white, and frequently of a different figure from what the same salts usually assume. The impure carbonate of ammonia, which is obtained by sublimation from bones, is rendered white, and is deprived of its fœtid odour by sublimation from an equal weight of charcoal powder. Malt spirit by distillation from charcoal is freed from its disagreeable flavour, though if too large a proportion has been used, part of the spirit appears to be decomposed, as is also the case in distilling vinegar with a similar addition. By mere maceration, in the proportion of about two ounces to eight or ten pounds, the flavour of the spirit is in eight or ten days improved. Water, which, from having been long kept in wooden vessels, has acquired an offensive smell, is deprived of it by filtration through charcoal powder, or even by agitation with it for a few minutes, especially when a few drops of sulphuric acid have also been added,—a process which may be employed to correct the fœtor water acquires in long voyages *. The fœtor even of putrid animal matter

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* Casks charred on the internal surface have been found to preserve water uncorrupted.—Nicholson's Journal, vol. xv, p. 226.

is removed by the admixture of charcoal. Resinous sub-
stances and balsams dissolved in alkohol, and subjected to
the action of charcoal, either by agitation with it, or filtra-
tion through it, are deprived of their colour, but not of
their peculiar smell. The smell of essential oils, either
pure or when they are dissolved in spirit, is not affected
by a similar process ; that of empyreumatic oils, however,
in a similar solution, as well as their colour, are complete-
ly destroyed. Distilled waters lose their odour, wines be-
come colourless, as do a number of the vegetable tinctures,
and of the lakes and pigments, as litmus, indigo, &c. when
dissolved in water ; and the gum-resins, opium, assafœtida,
&c. suspended in water, are deprived of their peculiar o-
dours. The astringency of vegetables appears to be im-
paired or destroyed by their infusions being digested with
a large quantity of charcoal *.

These experiments have been confirmed by other che-
mists, particularly by Brugnatelli, Westrumb, Gadolin,
and Kels †. I have made the experiment of the purifica-
tion of the fœtid carbonate of ammonia, above stated, and
found it perfectly to succeed. Some chemists, however,
Göttling, Hahneman and others, have not been successful
in repeating them, probably from the proper preparation
and the necessary proportions of the charcoal not having
been attended to. Lowitz has given several necessary
rules. The charcoal must have been well burnt, and
brought to a red heat before it is used ; it should be in
fine powder, and if not immediately used, carefully se-
cluded from the air ; and the requisite proportion must be
ascertained by experiments on a small scale, as, if too
little is employed, the effect will not be obtained, while,
in some cases, if there is an over-proportion, part of the

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* Crell's Chemical Journal, vol. ii, p. 165, 237.
† Ibid. 183.; vol. iii, p. 270.

substance designed to be purified is decomposed *. The
same charcoal may be repeatedly used, by keeping it for
some time in a state of ignition after it has been employed.

No satisfactory theory has been given of the action of
charcoal in producing these effects   That it is not me-
chanical. arising from its imbibing the matter it abstracts,
but chemical, is established not only by the nature of the
changes themselves, but by the decompositions produced
when it is used in large proportion.

The uses of charcoal are extensive.   As fuel it affords a
steady heat without smoke, and hence, in chemical expe-
riments, and in certain arts, as in dyeing, or in operations
on the metals, it is preferred to coal ; in metallurgic pro-
cesses, too, where it is employed to reduce metallic oxides
to the metallic state, it is more manageable and affords a
purer metal, though in this country, from the scarcity of
wood, coaked coal is generally substituted for it.   By
cementation with charcoal, iron is converted into steel.
It is used in the manufacture of gunpowder ; in its finer
state of aggregation, under the form of what are named
ivory black, lamp black, &c. it is the basis of black paints;
with fat oils, mixed with resinous matter to give due con-
sistence, it forms the composition of printing ink ; it is
used in various cases, from its property of destroying co-
lour and odour, and of resisting putrefaction ; and some
applications of it have been already taken notice of, from
its imperfect conducting power with regard to heat.

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* Crell's Chemical Journal, vol. ii, p. 270.

Sect. IV.—*Of Carbonic Acid.*

ALTHOUGH the formation and disengagement of this acid in chemical processes must have occasionally attracted the notice of chemists, no just idea was formed of its mode of existence, its nature, or properties, prior to its discovery by Dr Black. The accumulation of a noxious vapour in caverns and mines had indeed been frequently observed, as well as the production of a similar vapour in fermentation and combustion ; and this appears to have been regarded as a species of air by Van Helmont, Boyle, and Hales. The existence of such an aëriform or elastic fluid in mineral waters was also noticed by Hoffman, Venel, and Brownrigg ; and by the last chemist, in particular, its agency was investigated. But it was not clearly distinguished from other aëriform fluids : its characteristic qualities were not discovered ; nor its combinations, or its influence in chemical phenomena traced. These formed the objects of Dr Black's investigations ; important not only in themselves, but as having laid the foundation of Pneumatic Chemistry *. Brownrigg, Bewly and Bergman observed its acid powers, which are so weak as not to be very apparent. Cavendish and Priestley investigated several of its properties : And the fact having been observed by Black, that it is produced in the combustion of coal and charcoal, Lavoisier, in consequence of his theoretical views, was led to regard it as a compound of the inflammable matter of these substances with oxygen,—an opi-

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* They were first published in his Inaugular Dissertation, *De Magnesia Alba*, and afterwards in the 2d volume of the Edinburgh Physical and Literary Essays.

nion which he established by the combustion of charcoal
in oxygen gas.   It received from Dr Black the name of
Fixed Air, from other chemists the appellations of Aërial
Acid, Mephitic Acid, and Cretaceous Acid ; terms which
gave place to the preferable name of Carbonic Acid.

Carbonic Acid Gas may be said to exist in nature un-
combined. It is often accumulated in caverns and mines,
and forms that species of noxious elastic fluid, named
Choak Damp.   The Grotto del Cano, near Naples, is ce-
lebrated for the production of it.   In some mineral waters
it is so abundant, as to be disengaged when they issue from
the spring; and a small portion of it exists in atmospheric
air.   In a state of combination it is abundant.   The va-
rieties of Limestone, Chalk and Marl, and the Calcareous
Crystals, are compounds of it with lime : it is also com-
bined with some of the other earths, and is found as a con-
stituent principle of metallic ores.

It is generally obtained from any of the native carbon-
ates of lime, such as marble or chalk. If these be exposed
to a full red heat, the carbonic acid is dislodged from its
combination with the lime, and assumes the elastic form.
As the application of this high temperature is attended
with some difficulty, an easier process is to separate it
from its combination, by the action of a body exerting an
attraction to the lime.   A quantity of pounded marble or
chalk is put into a flask, to which a bent tube is adapted,
and sulphuric, or, what is preferable, muriatic acid, diluted
with water being poured upon it, a rapid effervescence
takes place, from the disengagement of the carbonic acid
gas.   It may be received over mercury or water ; by the
latter fluid, it is absorbed, but not immediately, in large
quantity, where agitation is not employed, and it is more
convenient operating with it than with quicksilver.   In
other processes in which carbonic acid is formed, as in
fermentation or combustion, it is either not pure, or not
disengaged in sufficient quantity, in a short time.

The direct formation of it is an important experiment, as determining its composition, and the proportions of its elements. It was performed by Lavoisier with much care. A piece of charcoal, of a determinate weight, was placed in pure oxygen gas, over quicksilver, and a very small bit of phosphorus being attached to the charcoal, it was kindled by a bent iron wire, heated red hot ; when the combustion had ceased, solution of potash was introduced, by which the carbonic acid gas was absorbed ; the diminution of volume in the oxygen gas was thus discovered, and of course the quantity of it which had entered into the composition of the carbonic acid ; and the remaining charcoal being likewise weighed, the loss of weight gave the quantity of it which had combined with the portion of oxygen spent in the combustion.

The results of the experiments were not uniform, and there was found a difficulty in determining the proportions, principally from the formation of a portion of water, from hydrogen existing in the charcoal, in consequence of which, when the weight of the carbonic acid gas estimated from its volume was compared with the weight of the oxygen and charcoal consumed, there was a deficit. Admitting a correction for this, the proportions in the first experiments were fixed by Lavoisier at 23.45 of charcoal, and 76.55 of oxygen ; but as determined by another experiment of a similar kind, which he selects as having been made under the most favourable circumstances, they were stated at 28.399 charcoal, 71.601 oxygen *. This was confirmed by avoiding the source of fallacy from the formation of water by operating on charcoal calcined by exposure for two hours in a covered crucible to a very strong fire, and which was presumed to contain no hydrogen. The experiment of this kind, which was regarded as the most accurate, gave the proportion of charcoal 28.888,

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* Mémoires de l'Acad. des Sciences, 1781, p. 452.

oxygen 71.11. Experiments were also made on the formation of carbonic acid in the combustion of wax, and in the combination of oxygen with charcoal from the decomposition of water, or of metallic oxides; the proportions were calculated in one experiment to be 69.675 oxygen, and 40.325 carbon; in another 71.78, and 28.22; but less dependence can be placed on these results, as they are attained by a more complicated method *.

The experiment was made by Clement and Desormes, apparently with considerable care, on charcoal thoroughly calcined, kindled by a lens in pure oxygen gas obtained from oxymuriate of potash. They fixed the proportions at 71.4 oxygen, and 28.6 pure charcoal †.

Messrs Allen and Pepys, in their experiments already noticed, employed every precaution to avoid any source of error; they found, that the diamond, and charcoal perfectly calcined, consume almost precisely the same quantities of oxygen in their combustion, and afford the same quantity of carbonic acid, and, as the average result, they state the proportions of the elements of carbonic acid at 28.6 carbon, and 71.4 of oxygen. which agree with those of Lavoisier, and also, as they have shewn, with those which may be inferred from the experiments of Tennant on the combustion of the diamond ‡.

Th. Saussure has since made the experiment of burning charcoal in oxygen to estimate the proportions of the elements of carbonic acid. He states them at 27.11 of carbon, and 72.89 of oxygen.

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* The above numbers were afterwards altered a little by Lavoisier, in consequence of finding the specific gravity of the oxygen gas to be rather greater than he had stated. But the alterations are not important, and the average may be regarded as he states it in his Elements, 28 of charcoal to 72 of oxygen.

      Annales de Chimie, tom. xxxix, p. 42.

   ‡ Philosophical Transactions, 1807.

In the conversion of oxygen gas into carbonic acid gas, by combination with charcoal, there is no change of volume. It had been supposed, indeed, in some experiments by Crawford and by Lavoisier, that there is a sensible condensation; but this had arisen from the presence of hydrogen or of moisture. Allen and Pepys found, that in operating on oxygen gas transmitted repeatedly over ignited charcoal so as to be converted into carbonic acid gas, the volume of gas at the end of the experiment was the same as at the commencement. And this has been confirmed by Saussure, Davy and Gay Lussac. This affords another method of determining the composition of carbonic acid, the difference in the specific gravity of the two gases giving the quantity of carbon. According to what appears to be the most accurate estimate of the specific gravities, the proportions will be 27.36 of carbon, and 72.64 of oxygen. Gay-Lussac states them at 27.38, and 72.62; and Dr Wollaston almost precisely the same. 100 of carbon, therefore, combine with 265, or 265.5 of oxygen.

As charcoal abstracts oxygen from all inflammable bodies, and appears therefore to have the strongest attraction to that element, it seemed difficult to effect the decomposition of carbonic acid, so as to establish its composition by analysis. It occurred to Mr Tennant, however, that this might be effected by the joint affinities of two elements. Phosphoric acid, in combination with lime, cannot be decomposed by heating it with charcoal; the united attractions of the lime to the acid, and of the phosphorus, which is the base of the acid, to its oxygen, being more powerful than the attraction of carbon for oxygen. If these attractions, therefore, are made to operate on carbonic acid, it may be decomposed. The experiment suggested by this idea was attended with success. Into a glass tube closed at one end, and coated with sand and clay, a little phosphorus was put, and over this a little carbonate of lime; the tube was then nearly, but not entirely closed.

Heat was applied to it, so that the middle of the tube was raised to a red heat. When cold, it was broken, and was found to contain a black powder, consisting of charcoal mixed with phosphate of lime *.

Dr Pearson found, that when the carbonic acid is combined with potash or soda, the decomposition of it is more easy and complete, as the attraction is not so strong as that to lime. With soda the attraction is weakest, and also a large quantity of carbonic acid is combined with it, so that a considerable quantity of charcoal may be obtained. Into a coated glass tube, closed at one end, were introduced 200 grains of transparent phosphorus ; and 800 grains of dried carbonate of soda were pressed down upon the phosphorus. The middle of the tube containing the alkali was heated red hot over a small furnace to within two or three inches of the phosphorus; and it was gradually drawn over the fire, and kept red hot for twenty minutes. The tube when cold was broken; a solid mass was found in the lower part of it as black as charcoal, weighing 428 grains, and above this a grayish matter, weighing 358 grains : on being thrown into boiling concentrated acetous acid, so as to saturate any soda, and dissolve the phosphate of soda formed, a quantity of pure charcoal remained, amounting when dried to 32 grains. It had no taste or smell, was extremely light, and by deflagration with nitre afforded carbonic acid †.

A similar result may be obtained in the humid way; if a piece of phosphorus be boiled in a solution of carbonate of soda, perfectly colourless, it becomes black and turbid, from the production of charcoal.

Carbonic Acid is decomposed by potassium. When it is heated in the gas, it burns, combining with the oxygen of the acid and precipitating charcoal : a small portion of carbonic oxide gas also remains, as Gay-Lussac and The-

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* Philosophical Transactions, vol. lxxxi, p. 182.
† Philosophical Transactions for 1792, p. 289.

nard have remarked ; potash with a little carbonate of po-
tash are formed. Potassium also produces charcoal when
it is heated in contact with carbonate of lime. A partial
decomposition of this acid, so as to convert it into carbonic
oxide, is likewise effected by those metals which have a
strong attraction to oxygen, as iron or zinc. When the
electric spark is taken in carbonic acid gas, by the me-
dium of an oxidable metal, as copper, there is a similar
decomposition and conversion of it into carbonic oxide,
the metal combining with the oxygen ; and even when pla-
tina wires are employed the acid is decomposed, and re-
solved into carbonic oxide and oxygen gases.

Carbonic acid contains no combined water, according
to the common expression of the fact ; that is, it is a bina-
ry compound of carbon and oxygen, with no hydrogen. No
water is deposited from it when it enters into saline com-
binations ; it can be formed from dry and perfectly cal-
cined charcoal, or, what is less ambiguous, from diamond
and dry oxygen. And when decomposed by potassium,
Gay-Lussac and Thenard found that there is no trace of
hydrogen *.

Carbonic acid gas is distinguished by its considerable
specific gravity ; it is about one-half heavier than atmo-
spheric air, and hence can be made to fall from a vessel
through the air. The precise specific gravity, compared
with atmospheric air, is, according to Biot and Arago, as
1.5196 to 1.0000. 100 cubic inches weigh 46.7 grains,
or, according to Allen and Pepys, 47.26 grains ; it is in-
odorous ; its taste is acid, with a degree of pungency. It
is incapable of supporting combustion, and proves speedily
fatal to animal life. Even when diluted with more than
twice its volume of atmospheric air, it can be breathed
only for a short time, as it produces giddiness and faint-
ness. It is formed in the respiration of animals, and is

* Recherches Physico-Chimiques, t. ii, p. 84.

contained in considerable quantity in the air they expire, as Dr Black in his investigation of its properties discovered by experiment.

Carbonic acid gas is absorbed by water; the water under a medium atmospheric pressure, and at a temperature of 50°, absorbing a quantity scarcely equal to its own bulk; this, however, is rather less than the real absorption. Dr Henry, avoiding the error which exists from the loose air of the water being expelled, and adding to the bulk of the residual gas, states that 100 cubic inches absorb at 60° 108 of gas. The absorption is promoted by agitation and cold. Under exposure to the atmosphere, the greater part of the gas slowly escapes, and at 212° the greater part or the whole of it is immediately expelled. Freezing also separates it. By augmenting the pressure, the quantity absorbed is increased, conformable to the law observed in the absorption of all aërial fluids. The water can thus be made to absorb three times its volume. When combined with an equal volume of the gas, it acquires an acidulous somewhat pungent taste, and sparkles when shaken. Its specific gravity is to that of distilled water as 1.0015 to 1000. It is rather singular, that an addition of saline matter to water diminishes its power of absorbing carbonic acid, and, in particular, a saturated solution of sea-salt does not absorb, according to Saussure, a third of its volume of carbonic acid, and requires for that a longer time than pure water does to absorb its own volume of the gas.

The acid powers of this gas, judging from its obvious properties, do not appear to be considerable. Its taste, either in its gaseous form, or combined with water, is slightly acidulous; it reddens none of the vegetable colours except the most delicate, the infusion of litmus*;

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* The infusion of litmus is reddened by a quantity of carbonic acid gas, not exceeding 150th of its volume, and one part of water saturated with the acid tinges red 50 parts of the

and it acts with no energy on inflammables or metals. It is superior, however, to the other acids in the power of neutralizing the alkaline properties; and hence Berthollet, in conformity to his views of affinity, supposed it to be superior to other acids in acidity, and ascribed its apparent weaker action to its elasticity. But its relation to the power of saturation depends, according to the theory of acidity which I have illustrated, to the relations in the combining weight of its radical, as has been already explained.

Carbonic acid combines with the alkalis, forming salts, named Carbonates. As the acid powers which it exerts are weak, the changes which it occasions in the properties of the alkalis are in general inconsiderable. They retain their peculiar taste and acrimony, to a certain extent; ammonia has still its penetrating odour, and in part its volatility; they change the vegetable colours to a green; they combine with oils, forming imperfect soaps, and the presence of the carbonic acid scarcely opposes any obstacle to the combinations of their bases with the other acids. The circumstance of the alkaline properties remaining in these compounds may be supposed to arise from their tendency to form with an excess of alkali, so that all of them, according to this view, may be regarded as subcarbonates. It is however uncertain, if by any definite proportion of carbonic acid, the alkaline properties can be completely neutralized; the odour and pungency, for example, of ammonia, always remain to a certain extent. The changes produced in the earths are more considerable, but still in some of them several of the original properties appear to be retained.

From this circumstance there is some difficulty in determining the constitution of these compounds, or what constitutes a carbonate and a subcarbonate. The exist-

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dilute infusion. The tint is fugitive, as the carbonic acid escapes when the liquor is exposed to the air.

ence in a crystallized form has been regarded as establish-
ing the distinction. The common subcarbonate of potash,
for example, cannot be crystallized, but is obtained by eva-
poration only in the state of a dry mass. If an additional
quantity of carbonic acid be combined with its base, it ac-
quires the property of crystallizing, and this crystallized
salt has been regarded as carbonate of potash. The cry-
stallized compound of soda and carbonic acid has likewise
been regarded as the carbonate of that alkali. But in both
these salts, the alkaline properties are predominant. The
case is the same with the compound of ammonia and car-
bonic acid; that which condenses from the combination of
carbonic acid and ammonia is evidently a subcarbonate;
and the analyses to be afterwards stated prove, that by dif-
ferent processes it may be obtained with various propor-
tions of its constituent parts.

Dr Wollaston found, as has been already stated, vol. i,
p. 124.), that when crystallized carbonate of potash, or of
soda, is exposed for a short time to a red heat, it passes in-
to a subcarbonate, which affords, when decomposed by an
acid, exactly half the quantity of carbonic acid gas which
the crystallized carbonate does. This appears, therefore,
to prove the existence of two compounds of determinate
composition, though in neither is the base neutralized. To
distinguish them Dr Wollaston, as has been already stated,
applied the terms Carbonate and Bi-carbonate. Berthol-
let, it has been remarked, (vol. i, p. 135,) in repeating this
experiment, obtained the same result; but he farther found,
that intermediate compounds may be obtained, and even
crystallized; and that there also exists a compound con-
taining less carbonic acid than the subcarbonate formed
from the decomposition of the carbonate at a red heat.

The distinguishing character of the carbonates and sub-
carbonates is their property of effervescing on the addition
of an acid, owing to the rapid disengagement of the car-
bonic acid, and its transition into the gaseous form. The

alkaline carbonates, as has been stated, retain the power of changing the vegetable colours to a green, and indeed, to a certain extent, nearly all the properties of their bases in their pure state. The carbonates of potash and soda are decomposed by a high temperature, as are also the earthy carbonates, the carbonic acid assuming the elastic form. The decomposition of the earthy carbonates requires a very high temperature, and neither in them nor in the alkaline carbonates is it easily rendered complete. It is facilitated by the admixture of charcoal, which converts the carbonic acid into carbonic oxide; and hence the explanation of a fact observed by Dr Black, with regard to carbonate of lime, and by Dr Hope with regard to carbonate of barytes, that the decomposition by heat does not succeed easily in an earthen, but with more facility in a plumbago crucible. It appears too, to be considerably influenced in some of these combinations by the presence of water, as has been already stated under the history of water, the water facilitating the expulsion of the acid by the affinity it exerts to the base.

The composition of the carbonates is determined by expelling the carbonic acid by a diluted acid, collecting and measuring its quantity from a given weight. The same weight of the compound is then exposed to a full red heat, by which both the carbonic acid and any water it contains are expelled : the difference between the loss of weight from this, and the weight of the carbonic acid in the first experiment, gives the quantity of water ; and the remaining weight is that of the base.

Carbonic acid in its gaseous state does not act on any of the metals, but water impregnated with it dissolves small portions of iron and zinc. By indirect methods it can be combined with metallic oxides, forming compounds the history of which belongs to that of the respective metals.

SECT. V.—*Of Hydro-Carbonic Acids.*

CARBON presents the singularity, compared with the other simple acidifiable bases, that it forms only one acid with oxygen, and that this acid does not, according to the common expression of the fact, contain any combined water : in other words, conformable to the theory of acidity which I have illustrated, that it forms only a binary acid with oxygen, and no ternary acid by the joint action of oxygen and hydrogen,—an anomaly somewhat striking, compared with nitrogen, sulphur, and phosphorus, from all of which acids both of binary and ternary composition are formed. There is a series of acids, however, from the vegetable kingdom, which are compounds of carbon, oxygen and hydrogen. These, in conformity to the theory of Lavoisier, were considered as composed of a compound radical of carbon and hydrogen acidified by oxygen ; but in conformity to the doctrine I have explained, their constitution as acids is that of carbon as a radical, acidified by oxygen and hydrogen. In this point of view, they have the same relation to carbon and carbonic acid, that nitric acid has to nitrous acid and nitrogen, or sulphuric acid to sulphurous acid and sulphur. And the only peculiarity is, that, apparently, from the more numerous proportions in which oxygen and hydrogen combine with carbon, there are a greater number of acids of this ternary constitution. The same laws exist with regard to them, as with regard to the others in the relations of the two common elements to the radical. In oxalic acid, for example, the proportion of the oxygen to the carbon is the same as that in carbonic acid ; and they differ, therefore, only in the former containing a definite proportion of hydrogen. In tartaric acid it is the same, only with a different proportion of hydrogen. In acetic acid, again, the proportion of oxygen to carbon is that

which constitutes carbonic oxide; and similar distinctions exist with regard to the others. In all of them, too, is displayed the general result, that acidity is more powerful from the joint action of oxygen and hydrogen on a radical, than from either of these elements alone.

Under this point of view these acids might be introduced in this part of the arrangement: But they are, on the whole, more strictly connected with the vegetable proximate principles; and while the characters of vegetable substances are admitted as grounds of chemical classification, it is proper to refer them to that class.

Sect. VI.—*Of Carbonic Oxide.*

CHARCOAL in burning becomes saturated with oxygen, forming carbonic acid ; and hence the existence of any intermediate compound was not suspected. It was discovered, however, that this acid, when exposed at a high temperature to the action of substances which havé a strong attraction to oxygen, is converted into a gas inflammable and having no acid properties,—a change apparently produced by the partial abstraction of oxygen. This gas therefore was regarded as an Oxide of Carbon. Berthollet supposed, that a portion of hydrogen exists in its composition ; but though there were some probabilities in favour of this, it has not been confirmed by subsequent investigation.

The discovery of this gas we owe to experiments suggested by some objections urged by Dr Priestley against the antiphlogistic system. He had observed, that in exposing to heat mixtures of gray oxide or scales of iron with charcoal, or with carbonate of barytes, large quantities of an inflammable elastic fluid are disengaged, which he regarded as analogous to the heavy inflammable air, or carburet-

ted hydrogen. His experiments were repeated by Dr Woodhouse of Philadelphia, and were confirmed, so far as related to the production of an inflammable elastic fluid *. Dr Woodhouse's memoir, transmitted to the French National Institute, had excited the attention of some of its members; a series of experiments on the subject was made by Berthollet †, and others by Clement and Desormes ‡. Prior to this, Cruickshank had entered on the investigation, and had established the principal facts as to the production and analysis of this elastic fluid ‖.

If, according to the original experiment of Priestley, a mixture of the gray oxide or scales of iron, and of charcoal, (each having been previously exposed in a covered crucible to a red heat, and the mixture of them made while they are hot,) be introduced into a coated glass retort, on raising it to a red heat a large quantity of elastic fluid is disengaged, which, as obtained at different stages of the process, is somewhat different. The first portion consists, according to Cruickshank, of one part of carbonic acid and four parts of inflammable gas; the second and third portions of one part with five, and after that to the end only one part of carbonic acid is found in seven of inflammable gas. The quantity in all, he remarks, is prodigious, —amounting to many gallons from two ounces of materials. A similar production of gas takes place, as Woodhouse ascertained, from mixtures of other metallic oxides, those of zinc, copper, lead, manganese or bismuth, with charcoal, treated in the same way. From the mixture with oxide of zinc, the proportion of carbonic acid to the inflammable gas, Cruickshank found to be less, being at first only 1 to 9, in a second portion as 1 to 26, and af-

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* Annales de Chimie, tom. xxxviii, p. 271.
† Mémoires de l'Institut Nationa
‡ Journal de l'Ecole Polytechnique, tom. iv, p. 323.
‖ Nicholson's Journal, 4to, vol. v, p. 3.

terwards what was received was purely inflammable. In general the oxides which retain their oxygen most strongly afford the largest quantity of inflammable gas ; and those which part with it readily the greatest proportion of carbonic acid. The latter is produced chiefly towards the commencement of the process, the former more abundantly, and in greater purity towards the end. Clement and Desormes found that the inflammable gas was produced by heat, from the mixture of a metallic oxide, as that of zinc, with charcoal thoroughly calcined, and also from the mixture of the oxide with plumbago or carburet of iron.

Supposing this gas to be an oxide of carbon, its production in these cases must be ascribed to the oxygen of the metallic oxide combining with the inflammable matter of the charcoal, the proportion not being such as to saturate the carbon and form carbonic acid.

The inflammable gas, freed from the carbonic acid by repeated washing with lime water, appears, as produced from these different mixtures, to be the same. It is very little higher than atmospheric air, its specific gravity being as 22 to 23 ; by this it is at once distinguished from the carburetted hydrogen gases, which in general are about one-half lighter than atmospheric air. It does not explode when mixed with atmospheric air and kindled, but burns with a blue lambent flame ; nor does it consume much oxygen in its combustion, 100 cubic inches of it weighing 30 grains, requiring for saturation only 44 cubic inches, or 15 grains of oxygen gas. The products, according to Cruickshank's estimate, are about 76 cubic inches, or 35.5 grains of carbonic acid, and 8 of water ; and its composition from this analysis he stated at 15 oxygen, 7 carbon and 1 hydrogen. Whether the hydrogen exists in combination with the carbon and oxygen of the gas, or in the state of a carburetted hydrogen mixed with the carbonic oxide, remained, so far as these results prove, uncertain.

The analysis of this gas, obtained from the mixture of oxide of zinc, and well calcined charcoal, by Clement and Desormes, afforded results somewhat different from those of Cruickshank. 100 measures of it required 35 measures of oxygen gas, and produced 81 measures of carbonic acid gas; whence, on the estimate that carbonic acid consists of 71.65 of oxygen, and 28.35 of carbon, they infer that carbonic oxide is composed of 58.4 oxygen, and 41.6 carbon by weight. These chemists produced the same gas, by exposing carbonic acid to a high temperature, in contact with charcoal; as, by heating a mixture of charcoal and carbonate of barytes, or by passing repeatedly carbonic acid, dried previously by exposure to muriate of lime, over charcoal ignited in a porcelain or glass tube.

Priestley had observed, that an inflammable gas is obtained by exposing to heat a mixture of carbonate of barytes, and gray oxide of iron. The experiment was repeated by Cruickshank, both substances having been previously made red hot, with the same result. When, in place of oxide of iron, he employed dry iron-filings, and mixed them with carbonate of lime (chalk,) which had been exposed to a low red heat, the mixture on being urged with heat afforded much more gas than the other, which at a mean consisted of 4 or 5 parts of inflammable gas with 1 of carbonic acid. A mixture of tin-filings and carbonate of lime gave a similar result. From clean zinc-filings, with carbonate of lime, a large quantity of gas was given out at a red heat, at first containing carbonic acid, but towards the middle and end of the process consisting of inflammable gas perfectly pure. This gas, from the manner of its production, might be expected to be a purer oxide of carbon than the preceding, as there is no source whence hydrogen could be obtained; for there is no reason to suppose the existence of water in carbonate of lime, and still less in that of native carbonate of barytes. It was

accordingly found by Cruickshank, that no sensible quantity of water is produced in its combustion.

He farther succeeded in obtaining it, by another process, in which it can scarcely be supposed to have received any hydrogen ;—decomposing carbonic acid in its elastic state. This was done in two modes : in one experiment, by placing at the bottom of an iron retort, a quantity of dry and very pure sand ; over this a stratum of chalk or carbonate of lime, which had been carefully dried ; above this another stratum of sand, on the surface of which was placed a quantity of very clean iron-filings. On raising the body of the retort to a red heat, gas was disengaged, which at first was chiefly carbonic acid ; but which as the process advanced, contained an increasing proportion of inflammable gas. In a second experiment, the conversion of the carbonic acid into carbonic oxide was effected by causing it to pass repeatedly through an iron-tube, filled with iron-wire, raised to a red heat ; by continuing this sufficiently long, three-fourths of the carbonic acid were converted into carbonic oxide. In both experiments the iron was oxidated, and they scarcely leave a doubt, but that by a partial abstraction of oxygen from carbonic acid, carbonic oxide is formed. In the first experiment, a little water might be supposed to be derived from the carbonate of lime which the iron would decompose ; and from which, therefore, a little hydrogen might be derived. But carbonic acid gas contains no sensible portion of water ; and in the second experiment, therefore, there is no source of hydrogen. And this experiment was repeated in a still more unexceptionable mode by Clement and Desormes, the gas having been, in order more completely to abstract the water, previously exposed to muriate of lime. It was almost totally changed into carbonic oxide.

The inflammable gas obtained from the decomposition of carbonic acid by the metals, is of the same specific gra-

vity as that produced from the mutual action of charcoal and the metallic oxides. It requires rather less oxygen for its saturation, and it does not, according to Cruickshank, afford any sensible portion of water in burning, while the other, when burnt in large quantity, deposited moisture on the sides of the vessel. From this, and from the fact, that the weight of the carbonic acid produced in the combustion of this gas, is, as near as can be expected, equal to the weight of the quantity of it and of oxygen consumed, he inferred, that it is a pure oxide of carbon. It appears, that carbonic oxide in burning combines with just half its volume of oxygen, and produces a quantity carbonic acid equal to its own volume. Cruickshank stated the proportion of oxygen lower; 100 measures of the oxide combining with 40 of oxygen, and producing 92 of acid: Mr Dalton estimated the proportion of oxygen at 47, and of carbonic acid 94 ; and Gay-Lussac and Berthollet have shewn, that the proportions of 100 of the oxide to 50 of oxygen by volume, forming 100 of carbonic acid, are the actual results * : 100 of carbonic acid contain exactly 100 of oxygen ; it follows, therefore, since 100 of carbonic oxide combine with 50 of oxygen, and form 100 of carbonic acid, that the oxide contains just half its volume of oxygen, and, of course, that oxygen doubles its volume in uniting with charcoal to form carbonic oxide. Reducing these proportions to weight, 100 of carbonic oxide are composed of 43 of carbon, and 57 of oxygen. This is the proportion of 100 of carbon with 132.5 of oxygen : in carbonic acid, as has been already stated, 100 are combined with 265.

Berthollet maintained the opinion, that this gas contains a small portion of hydrogen in its composition; and in support of this, stated, that when it is formed in the most unexceptionable mode, that of exposing native car-

* Mémoires d'Arcueil, tom. ii, p. 219.

bonate of barytes with iron-filings to heat, and when every precaution was taken to exclude moisture, still the carbonic oxide, in burning, afforded a small portion of water *. But this result might depend on the difficulty of entirely excluding humidity, more especially as it has not been confirmed by others.

Another circumstance from which the presence of hydrogen in carbonic oxide has been inferred, is its low specific gravity. Oxygen gas, combined with carbon, so as to form carbonic acid gas, has its density increased; yet by increasing the proportion of carbon, a compound is obtained not only lighter than the carbonic acid, but lighter even than the oxygen gas itself. This appears an anomaly in chemical combination, and it has been urged by Berthollet as such, and as a proof of his opinion, that carbonic oxide is not merely a binary compound of carbon and oxygen, but contains hydrogen. It has been explained by Dalton and Gay-Lussac, on the principle, that the carbon, in entering into the combination, assumes the gaseous form; and as its density in that state is not known to us, nothing strictly can be inferred as to the effect this ought to have in the combination; for it obviously does not follow, that when gaseous, its density must be superior to that of oxygen gas. And the condensation attending gaseous combinations being different in different proportions of the same gases, may give rise to the difference of effect in the formation of carbonic oxide and carbonic acid.

The properties of carbonic oxide gas, not noticed in the preceding part of its history, remain to be stated. Its specific gravity, as stated by Cruickshank, compared with atmospheric air, is as 957 to 1000. According to Clement and Desormes, it is .924; according to Dalton .945; and Gay-Lussac shews, from calculation, that it is .9678. It is absorbed in small quantity by water, 100 cubic inches

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* Mémoires d'Arcueil, tom. ii, p. 85.

of water absorbing 2.01 of the gas; or according to Dalton a larger quantity, the water taking up $\frac{1}{27}$ of its bulk. It is fatal to life when inspired; and from some experiments, appears to be peculiarly deleterious. It burns with a clear blue flame, and explodes feebly when previously mixed with atmospheric air, and kindled by the electric spark; the explosion is stronger with oxygen gas. The circumstances connected with this explosion of the gas are, as Mr Dalton has remarked, somewhat singular; it does not take place unless the carbonic oxide amount to at least $\frac{1}{5}$th of the mixture, and the oxygen must be at least $\frac{1}{13}$th of the whole. It even happens, when common air is used for oxygen, that an explosion takes place, and yet both carbonic oxide and oxygen remain in the residuum. When 100 measures of carbonic oxide are mixed with 250 of common air, an explosion is produced, but only $\frac{2}{3}$ds of the gas is burnt; the rest remains with a portion of oxygen *. Clement and Desormes supposed it to be decomposed, by passing it with a large quantity of hydrogen through an ignited glass tube, water being formed, and charcoal deposited; but according to T. Saussure, the appearance of carbonaceous matter is owing to the action of the hydrogen at this temperature, on the oxide of lead of the glass tube. It forms no combination with nitrogen, nor does it act on sulphur even in fusion. It appears to be capable of dissolving a small portion of melted phosphorus. It contracts no union with any of the alkalis, nor is there any reciprocal action between it and the acids.

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* Chemical Philosophy, p. 373.

Sect. VII.—*Of Carburetted and Oxycarburetted Hydrogen Gases.*

THERE are obtained, in various processes, inflammable elastic fluids, which, in their combustion, afford water and carbonic acid in different proportions, and which are therefore compounds of carbon and hydrogen, or of carbon, hydrogen and oxygen, and as such may have the common name of Carburetted Hydrogen, or Oxycarburetted Hydrogen applied to them. There is much difficulty in determining their composition, and there is even considerable uncertainty with regard to their specific distinctions. Two definite compounds appear to be established, both composed of carbon and hydrogen, and which, from their relative proportions, may be distinguished by the names of carburetted and supercarburetted hydrogen. Some chemists consider all the other gases of this family as mixtures of these with hydrogen and with carbonic oxide; while others maintain that carbon, hydrogen and oxygen may combine in more numerous proportions, and that some of these gases are ternary compounds of these elements. This question will fall to be considered after having given their leading distinctions. Dr Priestley first observed these elastic fluids. A series of experiments on their analysis was undertaken by Dr Austin[*], but the state of chemical knowledge at that period did not admit of their being sufficiently accurate. Cruickshank afterwards entered on the investigation of the subject, and though his conclusions with regard to their composition were erroneous, he established their distinctions, and ascertained a number of facts with regard to them[†]. The subject has

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[*] Philosophical Transactions, vol. lxxx, p. 51.
[†] Nicholson's Journal, 4to, vol. v.

since been prosecuted by Henry, Dalton, Berthollet, Dr Thomson, and T. Saussure.

Before proceeding to the history of these compounds, it may be remarked, that the same mode of analysis is applicable to all of them. It is that of detonation with a measured quantity of oxygen in a strong tube by the agency of the electric spark. After the detonation the diminution of volume is ascertained; the quantity of carbonic acid produced is discovered by its absorption by lime water, or an alkaline solution; the quantity of oxygen which remains is determined by a eudiometrical process, and thus the quantity is discovered which has been consumed. From the quantity of carbonic acid formed, we discover what quantity of the oxygen consumed had combined with carbon; this being facilitated by the circumstance, that oxygen gas suffers no change of volume in its conversion into carbonic acid, and therefore the volume of carbonic acid gives directly the volume of oxygen spent in its formation: what quantity has been consumed above this, it is inferred, must have combined with hydrogen, forming water; and the quantity of oxygen thus spent gives the quantity of hydrogen, calculating on the common estimate of the composition of water. If the quantities of carbon and hydrogen thus indicated are equal to the weight of the gas analysed, then it is inferred to be a compound of carbon and hydrogen in the proportions which the quantities of the products point out. If they fall short of the weight of the gas, some other element must have been present; and if no particular product appear corresponding to this, it is inferred to be oxygen, which has of course entered into the composition of the water or carbonic acid, and the quantity may be inferred from the difference of weight.

This mode of analysis, which is important from its connection with the vegetable analysis, may be illustrated from the following table, which exhibits the results of Dr Henry's experiments on these gases.

Kind of Gas.	Oxygen Gas saturating 100 Measures.		Carbonic Acid produced.
Pure hydrogen, -	50 to 54		
Gas from moist charcoal,	60	-	- 35
———— wood (oak), -	54	-	- 33
———— dried peat, -	68	-	- 43
———— coal, or cannel,	170	-	- 100
———— lamp oil, -	190	-	- 124
———— wax, -	220	-	- 137
Pure olefiant gas, -	284	-	- 179

" If it be assumed, that in the formation of each measure of carbonic acid, in the above experiments, an equal volume of oxygen gas is employed, we learn, by deducting the numbers in the third column from the corresponding one in the second, what proportion of the consumed oxygen has been allotted to the saturation of the hydrogen of each hydro-carburet. Thus, in the combustion of the gas from coal, 70 parts of oxygen have disappeared, besides that which has entered into the carbonic acid; and, since each measure of oxygen saturates two of hydrogen gas, the gas from coal must contain, in 100 measures, a quantity of hydrogen, which, expanded to its usual elasticity, would occupy 140 measures. By a similar mode of estimation, the quantity of hydrogen in other species of inflammable gas may be ascertained, viz. by subtracting the number in the third from the corresponding one in the second column, in each instance, and doubling the remainder [*]."

Dr Henry found, that in this method by detonation, there are sources of error which render the results uncertain. He therefore proposed another, in which a stream of the inflammable gas is made to burn in oxygen gas; a larger quantity can thus be operated on; and the quantities of oxygen gas consumed, and of inflammable gas burned, can, by the nature of the apparatus, be accurately as-

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[†] Nicholson's Journal, vol. xi, p. 66.

certained. One farther step is necessary; for during the burning, part of the inflammable gas escapes unconsumed, and mingles with the residual air. The quantity of this is ascertained, by rendering the mixture of it with the residual oxygen capable of detonating by the addition of a known volume of pure hydrogen, and ascertaining the consumption of oxygen in this detonation, and the products[*].

In all these gases Berthollet found nitrogen gas, whether derived from atmospheric air or not is uncertain. The oxygen of any portion of atmospheric air mixed with them cannot be discovered by the sulphuretted hydrosulphurets, for the inflammable gas is absorbed by these liquors, but it is indicated by nitric oxide; the quantity is not proportional to that of the nitrogen, which remains after the analysis by detonation.

Another mode of analysing these gases is that by the action of oxymuriatic gas, which imparting oxygen to them converts them into water and carbonic acid; or if the proportion of oxymuriatic gas be deficient, with the production in some of them of carbonic oxide. The slow action whence these changes arise is materially influenced by the agency of light. If the electric spark be taken in the mixture of the two gases over water, an explosion happens, there is a production of carbonic and muriatic acids; and from some of the gases, particularly when the proportion of oxymuriatic acid is deficient, a deposition of charcoal takes place[†]. Carbonic oxide gas, mixed with oxymuriatic acid gas, cannot be exploded or inflamed by the electric spark, and this affords a distinction between it and the above described gases.

The first gas of specific composition, and to which the name of Carburetted Hydrogen is more peculiarly appropriated, is one not obtained by an artificial process. It is

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[*] Philosophical Transactions, 1808.
[†] Nicholson's Journal, 4to, vol. v, p. 202.

the elastic fluid which arises from marshes, and which is evidently produced from the decomposition of vegetable matter. It had been observed by Cruickshank, and has been particularly examined by Mr Dalton *, and by Dr Thomson †. It has always an intermixture of nitrogen and carbonic acid gases. The quantity of nitrogen, Dalton states, is sometimes so much as 20 *per cent.* Dr Thomson did not find it so considerable : the proportion of atmospheric air and carbonic acid together sometimes amounted to 20 *per cent.*, and the proportion of atmospheric air appeared to be always uniform, amounting to 12.5 *per cent.* or 2.5 of oxygen and 10 of nitrogen. The quantity of carbonic acid varied from 5 to $7\frac{1}{2}$ in 100 parts. When these are abstracted, the gas is of uniform constitution and properties. It is colourless, transparent, and when washed with water inodorous. Its specific gravity, according to Mr Dalton, is very near .6 ; according to Dr Thomson, .611, and when freed from atmospheric air, it is by calculation .5554 ; 100 cubic inches weigh 16.93 grains. Water absorbs $\frac{1}{27}$ of its bulk. It burns with a yellow flame, which, Dr Thomson remarks, is larger than that from any other of these gases, except olefiant gas, and the gas from ether. It does not explode readily when the electric spark is sent through its mixture with atmospheric air ; it requires, as Dalton has stated, the proportion of 10 parts of the air to 1 of gas, and the detonation is feeble. With oxygen gas it is more powerful, still requiring however a certain proportion to produce this. According to Dr Thomson it does not detonate unless the bulk of the oxygen rather exceeds its own bulk, and it ceases to do so when the oxygen gas is more than $2\frac{1}{2}$ times the bulk of the inflammable gas. In mixture with atmospheric air, not less of the inflammable gas than $\frac{1}{12}$ of the volume of common air

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* System of Chemical Philosophy, p. 444.
† Transactions of the Wernerian Society, vol. i.

must be present to produce explosion; and when it exceeds
$\frac{1}{8}$th of the volume of the air, the mixture ceases to explode.

When the proportions are adjusted for complete inflam-
mation, 100 measures of it consume, according to Dr Thom-
son, 205 measures of oxygen gas, and 104 measures of car-
bonic acid gas are formed; or rather, what seems more ac-
curate, 100 consume 200, and form 100 measures. A gi-
ven volume of carbonic acid gas containing the same vo-
lume of oxygen gas, this quantity of the oxygen consumed
must have combined with the carbon of the carburetted hy-
drogen, and the remainder of the oxygen must have com-
bined with the hydrogen of the gas to form water. From
these conclusions Dr Thomson inferred, that 100 cubic in-
ches of it are composed of 13.24 of carbon, and 5.17 of hy-
drogen, or 100 by weight are composed of 72 of the former
and 28 of the latter. Mr Dalton stated the proportions
of 73 and 27. Admitting the correction, according to the
more accurate estimate, in the proportion of oxygen con-
sumed and carbonic acid formed, with the just specific gra-
vities of the gases, they may be stated at 74 and 26,—a re-
sult which establishes a conformity, according to the law of
multiples, with the proportions in the other definite com-
pound, supercarburetted hydrogen.

This gas is decomposed by electricity; charcoal is depo-
sited, the gas almost doubles itself in volume, and, accord-
ing to Mr Dalton, becomes pure hydrogen.

The gas which arises from coal mines, which is known
by the name of Fire Damp, and is often the cause of acci-
dents by its explosion, was observed by Dr Henry to be
this species of carburetted hydrogen *. It is usually mix-
ed with carbonic acid gas, and probably originates in the
decomposition of water transuding through the coal. From
its low inflammability it seems to be kindled with explo-
sion in the mine only from the large mass accumulated,

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* Nicholson's Journal, vol. xix, p. 149.; xxii. p. 98.

aided, perhaps, by the pressure. Hence the principle of the Safety Lamp of Sir H. Davy, already explained, (page 78,) in which, by a covering of wire gauze, the kindled gas within the lamp is so far reduced in temperature, in passing through, that it does not kindle the gas without. From the greater levity of the gas, it accumulates chiefly in the roof of the mine ; and on this depends the security of a Lamp which I suggested, in which a current of air to support the flame within a close lantern is supplied by a tube from the floor, or if necessary from any of the passages of the mine *.

The associated Dutch Chemists discovered another compound inflammable gas, which, from a peculiar property it has of affording, when acted on by oxymuriatic gas, an oily-like product, they named Olefiant Gas. It constitutes a species of definite composition, and from containing more carbon than the former, has received the name of Super-carburetted Hydrogen. It is formed in the common process of preparing sulphuric ether, by exposing to heat a mixture of equal parts of sulphuric acid and alkohol. They observed, that towards the end of the formation of ether, this gas is produced; and by taking the proportions of acid and alkohol which exist at this period, consisting of from 3 to 4 of sulphuric acid to 1 of alkohol by weight, it may be produced in abundance without ether being formed. The alkohol is put into a retort, and the acid poured upon it ; on mixing them by agitation, the fluid becomes warm, and acquires a brown colour ; gas begins to be disengaged, the formation of which is accelerated by applying a moderate heat. It is received over water, and consists of sulphurous acid and a little carbonic acid, mixed with olefiant gas ; the former are abstracted by agitation with water, to which a little lime or ammonia has been added. The olefiant gas is then obtained pure †.

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* Transactions of the Royal Society of Edinburgh, v. vi, p. 31.
    † Nicholson's Journal, 4to, vol. i, p. 44.

The specific gravity of this gas is much greater than that of the preceding gas, being to that of atmospheric air, according to Henry, as 967 to 1000; according to Dr Thomson 974; according to Saussure 985. 100 cubic inches weigh 29.8 grains.   Its odour is slightly foetid ; it is absorbed by water, the water condensing about $\frac{1}{8}$ of the bulk of the gas. It burns with a strong dense oily-like flame, and when previously mixed with oxygen, and a spark sent through the mixture, detonates with great violence. It is decomposed, according to the Dutch chemists, by being passed through an ignited porcelain tube, and is converted into an inflammable gas much more rare, with a deposition of charcoal, and a production of carbonic acid [*].   Berthollet did not obtain the last product, and according to Dr Thomson there is no production of carbonic acid if the common air has been expelled from the tube by a current of hydrogen gas, and the olefiant gas is pure.

Oxymuriatic gas exerts upon it a singular action, changes its composition, and condenses it into a liquid, having the appearance of oil. The circumstances of this decomposition belong to the history of oxymuriatic acid.

The analysis of this gas is effected by its combustion, though this is difficult or scarcely practicable in the usual mode by the eudiometer of Volta, from the violence of the detonation, by which even the strongest tubes are liable to be broken. This is best prevented by employing a much larger quantity of oxygen than the olefiant gas can consume, 500 measures of the former, for example, to 100 of the latter : this dilutes the gas so much that the detonation is less violent, and it is easy to discover from the residuum what quantity of oxygen has been spent. Of any of these gases, it requires the largest quantity of oxygen for its combustion, a proof that in a given volume it contains the largest quantity of inflammable matter, and a

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[*] Nicholson's Journal, 4to, vol. i, p. 54.

proof therefore of the condensation of its elements. According to Berthollet, 100 measures require for saturation 280 measures of oxygen gas, and produce 180 of carbonic acid *. Dr Henry found, that 100 measures require 284 of oxygen, and produce 179 of carbonic acid; but afterwards he stated, as the results of the method by slow combustion, 100 measures consuming 325 of oxygen, and producing 200 of carbonic acid †. Mr Dalton found the consumption always less than 300, and the production of acid 185 or 190. And Dr Thomson found, that 100 measures consume, on an average, 302 measures of oxygen, and form 208 of carbonic acid : while the results of Saussure's experiments approach nearer to those of the former, 100 measures consuming 292 of oxygen, and forming 201 of carbonic acid. From the laws which regulate the combination of gases, and the condensation which attends it, it may be inferred from these results, that 1 measure of olefiant gas requires 3 measures of oxygen for its combustion, and forms 2 measures of carbonic acid ; and from this it follows, that it is composed of 85 of carbon, and 15 of hydrogen. Saussure had stated them at 86 and 14. But from a more recent analysis, he assigns those of 85.03 and 14.97 ‡. Taking the proportions in carburetted hydrogen at 74 of carbon and 26 of hydrogen, and in super-carburetted hydrogen at 85 and 15, the usual law of multiples in chemical combination is observed, 100 of carbon being combined in the one with 17.6 of hydrogen, and in the other with twice that quantity, 35.2.

Olefiant gas is decomposed by electricity, charcoal is precipitated, and hydrogen gas is evolved, equal nearly to double the volume of the former gas, 40 measures of ole-

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* Mémoires de l'Institut National, tom. iv, p. 298.
† Philosophical Transactions, 1808.
‡ Annals of Philosophy, vol. iv, p. 38.

fiant gas, according to Dalton, becoming 78 of hydrogen. This may be regarded as a proof that it contains no oxygen, as if that element were present it ought to appear in the form of water or carbonic oxide.

It was observed by Cruickshank and Berthollet with regard to the detonation of olefiant gas, that when an inferior proportion of oxygen is used, as that of 3 measures with 4 of the olefiant gas, the combustion is comparatively feeble; a little water is formed, with frequently a trace of carbonic acid, and a portion of charcoal deposited. But instead of there being any diminution, there is a considerable increase of volume, 100 measures of the mixture expanding nearly to 180. This residual gas, Berthollet regarded as a compound of oxygen, carbon and hydrogen : Mr Dalton considers it as a mixture of carbonic oxide and hydrogen; part of the oxygen in the detonation combining with the carbon, and converting it into carbonic oxide, and the greater part of the hydrogen being set free.

Besides the two compounds of carbon and hydrogen now described, there are a number of other elastic fluids containing these elements, the precise characters and composition of which are not so easily determined. The gas of this kind which has been longest known, and which indeed is the first that was discovered, is obtained in the decomposition of water by charcoal at a red heat. It was discovered by Priestley, who gave it the name of Heavy Inflammable Air : it was afterwards named, from its composition, Hydro-Carbonate. The process by which it is obtained consists in placing small pieces of charcoal in an earthen or iron tube, which is raised to a red heat by being placed across a furnace, and, by means of a funnel connected with one extremity of the tube, the aperture of which is nearly closed with a screw, water is dropt upon it slowly, so that the vapour shall pass over the ignited charcoal; a quantity of gas issues from the other extremi-

ty of the tube, which may be collected over water. It consists of carbonic acid gas and the inflammable gas; the former can be abstracted by agitation with water, in which a small quantity of lime is suspended; the inflammable gas remains pure.

The production of this gas is evidently owing to the decomposition of the water; and one portion of the oxygen of the decomposed water forms carbonic acid, while the hydrogen unites with the carbon. But a part also of the oxygen exists in the composition of the inflammable gas, as is found by its analysis. And in a certain relative proportion of the water to the ignited charcoal, scarcely even any carbonic acid was found by Cruickshank to be formed. To determine its composition, he submitted it to detonation in mixture with oxygen by the electric spark, 100 cubic inches weighing 14.5 grains consumed 66 cubic inches of oxygen weighing 22.4 grains, and produced 40 cubic inches of carbonic acid weighing 19 grains, with a quantity of water deposited equal to 9 grains, besides a quantity held in solution. From these results Cruickshank inferred, that the inflammable gas consists of 4 of carbon, 1.3 hydrogen, and 9 water. It is evident, however, that no such quantity of water can pre-exist in it, and the conclusion to be drawn is, that the elements of this water, the oxygen and hydrogen, exist in the gas, with the proportion of hydrogen which Cruickshank assigns, the oxygen being either in direct combination with the carbon and hydrogen, or being in the state of carbonic oxide mixed with carburetted hydrogen. Berthollet, adopting the first view, that is, considering it as a ternary compound, or oxycarburetted hydrogen, stated its composition, from the results of his own experiments, at 43.91 of charcoal, 33.61 of oxygen, and 22.48 of hydrogen [*].

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[*] Mémoires d'Arcueil, t. ii, p. 93.

The specific gravity of this gas has been stated to that of atmospheric air as .48 to 100; but it varies much : by Berthollet, it is stated as low as .26, which shews the very various states in which these gases exist when obtained even by the same process, and so far proves that they are either disengaged in a state of intermixture, or that they must be of very various composition. When kindled, it burns with a blue lambent flame; 100 measures of it combine in burning with about 66 of oxygen. During its combustion, a considerable quantity of water is deposited on the sides of the vessel, and the residual gas is carbonic acid.

The gas which is expelled from charcoal alone by heat appears to be of a similar nature. It varies, however, a good deal at different stages of the process, becoming lighter as the operation proceeds, so that the gas expelled at the end in Berthollet's experiments had a specific gravity of only 0.18, while that at the beginning was equal to 0.46.

The gas from humid charcoal is eminently fatal to animal life. Breathed pure, it occasions immediate death, and diluted with 20 parts of atmospheric air it is strongly depressing; it reduces the force of the circulation, causes nausea and vertigo, and if breathed too long, suspension of the vital functions,—effects probably owing to its chemical action on the blood. A singular fact, exemplifying this action, has been taken notice of by Dr Beddoes, that venous blood exposed to it assumes a vivid florid hue, similar to that of blood in the arterial state.

In the decomposition of certain vegetable products by heat, other species of gases are obtained, varying in their composition, as to the proportions of their elements, and containing in general more carbon. One formed by passing the vapour of camphor through a red-hot tube, is considerably heavier than that from humid charcoal, and requires more than double the quantity of oxygen to saturate

it, 100 measures combining with 176 of oxygen gas ; this gives as the products, according to Cruickshank's experiments, 116 measures of carbonic acid gas, weighing 54.5 grains, 18 grains of water deposited, and 8 or 9 which he supposes to have been held in solution ; whence he inferred that it consists of 11 carbon, 2 hydrogen, and 8 or 9 of water. Berthollet states its composition to be 48.63 of carbon, 25 35 of oxygen, and 26.02 of hydrogen. Other gases somewhat analogous were obtained by the associated Dutch Chemists, by passing the vapour of alkohol or of ether through an ignited glass tube *. Both are rather lighter than that from camphor. That from alkohol they state to have a specific gravity to that of atmospheric air, as 0.436 to 1000. It burns with a pale blue flame, similar to that of alkohol. The gas obtained by passing the vapour of sulphuric ether through an ignited tube, is, according to the Dutch Chemists, heavier than that from alkohol, its specific gravity being to that of atmospheric air as 6.709 to 1000,—a distinction between them which Cruickshank also observed, the specific gravity of the one, that from alkohol, according to him, being to that of atmospheric air as 12 to 23 ; of the other, that from ether, only as 15 to 23. It burns too with a more dense and oily like flame, of a blue colour, and requires for its saturation a greater quantity of oxygen. Saussure, who had formerly given an inaccurate analysis of these gases, has more lately submitted them to examination. The gas from alkohol consists of carbon 57.574, oxygen 28.466, hydrogen 13.960 : the gas from ether of carbon 63.86, oxygen 22.01, hydrogen 14.13. In the analysis of both of them he found the striking result, that the oxygen consumed is to the carbonic acid produced as three to two : this is the case with olefiant gas, and

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* Nicholson's Journal, 4to, vol. i, p. 52.

therefore these gases are composed of the elements of olefiant gas and water *.

Gases are obtained in some other processes, which approach still more nearly to olefiant gas in their characters and composition, and which perhaps consist chiefly of it with some intermixture. The Dutch chemists discovered the singular fact, that a gas of this kind is formed, by passing the vapour of alkohol, or of ether, through an ignited tube of pipe clay, while it is not formed in an ignited glass tube. If, in the glass tube, however, a quantity of siliceous or aluminous earth be put, on raising it to a red heat, and passing the vapour of alkohol or ether over it, there is a production of this gas. The same effect is not obtained when lime or magnesia has been put into the glass tube. The precise explanation of these facts is difficult, but the effects depend probably on the different powers of the different substances of communicating temperature ; a slight variation in the temperature, communicated to the vapour in its rapid passage through the tube, varying the affinities of its elements, and determining their combination in various proportions. This is confirmed by the remark by Saussure, that nothing is more variable than the composition of these gases, according to the degree of heat, the diameter of the tube, and the period of the experiment at which they are collected.

A gas of a similar nature appears to be produced in the decomposition of wood and other vegetable substances by heat. A quantity of oil is produced even where the substance decomposed is not of an oily nature; and the inflammable gas which is disengaged burns with a dense oily-like flame like the olefiant gas, and deposites a quantity of charcoal, if the supply of air be not very rapid and abundant.

Gases are obtained from oil and wax decomposed by heat,

* Annals of Philosophy, vol. iv, p. 34.

which resemble the olefiant gas, in the great illumination produced by their combustion, arising no doubt from the same cause, the condensation of their elements. These gases are produced in the common mode of burning oil, tallow, and wax, the heat present in the wick decomposing the unctuous matter ; but their combustibility, or rather the quantity of light afforded by their combustion, is also probably increased by a portion of oily matter in vapour mixed with the gas. The specific gravity of the gas from oil decomposed by a red heat, Berthollet states at 0.348, and its analysis gave as the proportions of its elements 52.09 of carbon, 24.03 of oxygen, and 23.88 of hydrogen.

The gas which has been procured from coal by the application of heat, and applied to the purpose of obtaining artificial light, is so far analogous to these gases, that it burns with a very dense oily like flame, and it produces much more illumination than pure hydrogen, or the carburetted hydrogen obtained in the decomposition of water by charcoal. Dr Henry also found, that in its combustion more oxygen is consumed, the quantity being inferior only to that which is required in the combustion of the pure olefiant gas, and in that of the gases obtained from the decomposition of oil and wax by heat. It is mixed with variable portions of carbonic acid and sulphuretted hydrogen, which may be abstracted by agitation, with solution of potash ; and it contains in general also a portion of olefiant gas, which may be discovered by its condensation by the action of oxymuriatic gas. But by far the greater part of it, amounting generally to 96 or more in 100 parts, is, according to Dr Henry's experiments [*], a peculiar gas, which is not affected by any of these agents, which is therefore different from olefiant gas ; and is not easily reduced to any known species. It varies, too, as obtained from different coals, and even at different stages of the process, in

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[*] Philosophical Transactions, 1808.

general diminishing in its power of illumination as the process proceeds. And from some coals the gas evolved is lighter than any known species of carburetted hydrogen, being only .187 or .190, atmospheric air being 1000, while that of the inflammable gas from humid charcoal is .600 : the specific gravities of other coal gases vary from .300 to .780. Its application to the purpose of procuring illumination on a large scale, originally introduced by Mr Murdoch [*], has been attended with complete success. The general outline of the method is to submit coal to a red heat in iron cylinders or retorts. The gas is disengaged with a considerable quantity of bituminous matter, or coal tar ; this is received in a condensing vessel ; and to abstract it as much as possible, the gas is farther conveyed through vertical tubes kept cool by being surrounded with cold water, by which an additional portion of the tar is condensed. It is then passed through water, in which slaked lime is diffused, and is agitated with it, by which the sulphuretted hydrogen, carbonic oxide and carbonic acid are absorbed ; and the inflammable gas remains pure. It is lastly received in a large reservoir constructed as a gazometer, from which a main pipe issues, and is conveyed by branches to tubes with small apertures furnished with stopcocks, at the extremity of which it is allowed to burn. When it has been properly purified, the light it affords is clear and brilliant, much superior to that afforded in any other mode ; and as the coak from the coal is of value, the method is also superior in economy to any other.

There have thus been described a number of gases containing carbon and hydrogen, and in the greater number of them a proportion of oxygen, varying in their properties, and in the proportions of their elements. The ques-

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[*] Philosophical Transactions, 1808.

tion remains for determination, Are they of definite composition, and to what precise species can they be reduced?

The two species of carburetted hydrogen first noticed, the marsh gas and the olefiant gas, seem to be definite compounds, composed of carbon and hydrogen alone. The uncertainty is principally with regard to the others,—those in which oxygen also exists. Two opinions have been proposed with regard to their constitution. They may be considered as oxycarburetted hydrogen gases, that is, as ternary compounds of carbon, hydrogen and oxygen : Or, according to an opinion maintained by Mr Dalton and Dr Henry, the oxygen they contain may exist in the state of carbonic oxide, and the whole of them may be mixtures of the two species of carburetted hydrogen, with carbonic oxide, and sometimes a portion of pure hydrogen.

There is reason to believe that they are sometimes evolved in a state of mixture. Dr Henry gives as a proof of this a fact observed by Cruickshank, that some of these inflammable elastic fluids afforded different quantities of carbonic acid in burning, according as they had been previously washed with water or not, although the original gas contained no carbonic acid,—a fact best explained on the supposition that the gas had contained a portion of olefiant gas, which being more soluble in water than the others, would be removed by the washing, and from the large proportion of carbon it contains, less carbonic acid would be produced by the combustion after its removal than when it was present. Another fact which has been considered as proving the presence of olefiant gas is the rapid diminution of volume to a certain extent from the action of oxymuriatic gas. It is probable that portions of carbonic oxide may sometimes also be evolved. This much may be admitted ; but still it does not follow that all the diversities among these gases arise from such intermixtures, and there are some which cannot be satisfactorily accounted for on such an hypothesis.

Thus, some of these gases, those evolved in particular from some kinds of coal by heat, are much lighter than the lightest of the two species of carburetted hydrogen, the marsh gas. Its specific gravity, atmospheric air being 1000, is 555. But the gas from humid charcoal is not more than 480, and that evolved from coal is usually below 500, and is sometimes so low as 350 or 300. To account for this, it is supposed that these gases are mixtures of carburetted with pure hydrogen. But Berthollet has justly remarked, that it is a supposition altogether gratuitous that hydrogen in a pure form exists in any of these gases; and it is one extremely improbable, considering the affinity of this element to carbon, that it should be disengaged pure from substances containing carbonaceous matter. It is more probable that these gases contain both carbon and hydrogen in direct combination; and as there is a series of them of numerous degrees of specific gravity, from .600 to .300, this proves that these elements may combine in several proportions between these extremes, and affords grounds from analogy to draw a similar conclusion with regard to those gases which are of greater specific gravity. With regard to the intermixture of olefiant gas, as another source of the diversity of properties in these gases, it is also a just observation by Berthollet, that as it is decomposed at a red heat, its presence can scarcely be supposed in gases which have been formed at or above that temperature.

The peculiar energy of action on the living system of the gas disengaged from humid charcoal at a red heat, proves it also to be a compound of specific composition, and not, as is supposed, a mixture of carburetted hydrogen and carbonic oxide, for its powers are in no respect intermediate between these, but much superior to either.

Mr Dalton admits that the gas from charcoal always contains oxygen; but then this oxygen, he supposes, is united to the carbon, forming carbonic oxide: the rest of

the mixture consists of carburetted hydrogen and hydrogen; and he adds, that he never finds any difficulty in ascertaining the relative quantities of each of the gases in such mixtures. No doubt, if it be assumed that these gases are mixtures, it may be easy, from the products of their analysis, to infer, what proportions of hydrogen, carbonic oxide, &c. they must according to the hypothesis consist of. But this is no proof that they are such mixtures; nor has any such proof been given, at least to establish the hypothesis in all the extent in which it is maintained. The facts above stated appear irreconcilable with it; and the consideration, that the affinities of carbon, hydrogen and oxygen, are actually balanced in natural products, so that they are united in very numerous proportions, renders more probable the opinion, that in the formation of these compound gases, they may, to a certain extent at least, obey a similar law.

The greater levity of some of these gases, than of the carburetted hydrogen or marsh gas, leads to the conclusion, that there probably exists a definite compound of carbon and hydrogen, with a still lower proportion of carbon than what is assigned to its composition. Or perhaps such a gas of low specific gravity may in common, with some of the others, be a ternary compound of carbon, hydrogen and oxygen.

The gases obtained from the decomposition of alkohol and ether by heat must, if the results stated by Saussure be correct, be definite compounds of carbon, hydrogen and oxygen. In both of them, as has been already stated, the volume of oxygen which they consume in their combustion is to that of carbonic acid formed as three to two. The same law exists with regard to olefiant gas. There is, therefore, in these gases, merely an addition of water, or rather of the elements of water to the elements of olefiant gas; and they may be represented by certain portions of these two compounds. And this he found to be the case,

even when they varied somewhat in composition from the circumstances of their production, the variation amounting only to differences in the relative quantities of these two binary compounds. Taking the proportions of the gas from alkohol, as already stated, 57.574 of carbon, 28.466 of oxygen, and 13.960 of hydrogen ; this quantity of oxygen forms 32.237 of water, and there remains an excess of hydrogen above what furnishes this, of 10.189, which, with the quantity of carbon that is present, forms exactly the constitution of olefiant gas. In like manner, taking the proportions of the gas from ether, 63.86 of carbon, 22.01 of oxygen, and 14.13 of hydrogen ; this quantity of oxygen forms, with the due proportion of hydrogen, 24.93 of water, and there remains an excess of 11.21 of hydrogen, which, with 63.86 of carbon, form olefiant gas. The gas from alkohol is represented by 2 of olefiant gas, and 1 nearly of water by weight, or by 100, and 47.6 : the gas from ether by 3 of olefiant gas, and 1 of water in weight.

There is no mode of considering this, but by admitting that these gases are ternary compounds of carbon, hydrogen and oxygen in definite proportions. They are therefore oxycarburetted hydrogen gases.

Sect. VII.—*Of Carburetted Sulphur.*

THIS singular substance, with regard to the nature of which the most discordant opinions have been maintained, was discovered by Lampadius, a German chemist, in submitting to heat a mixture of charcoal and native sulphuret of iron. He failed in attempting to repeat the experiment; but after an interval of some years, he succeeded in procuring a similar product by distillation from

wood impregnated with pyrites; and he found it also to be formed on exposing a mixture of pyrites with bituminated, or even with common wood, in a retort to a red heat. Alongst with a production of sulphuretted hydrogen, a fluid distilled over, which, sunk in water placed in a receiver connected with the retort, and which, when obtained pure by a second distillation with a gentle heat, was found to have a penetrating odour, to be highly volatile, so as to boil at 104°, and produce cold in its spontaneous evaporation, inflammable, and yielding, in its combustion, sulphuric acid and water, soluble abundantly in alkohol, and very sparingly soluble in water. This substance he named Alkohol of Sulphur from its volatility, and he considered it as a compound of sulphur and hydrogen *.

Clement and Desormes, in experiments undertaken to examine the nature of charcoal, obtained a similar product. Their process consisted in passing sulphur in vapour through an ignited porcelain tube, in which fragments of charcoal had been previously heated, this previous heat having been applied until the product of gas which charcoal alone affords had ceased, and the sulphur being then introduced slowly. A yellowish liquid condenses in the vessel adapted to the extremity of the tube, similar in its properties to the liquid obtained by Lampadius. No gas is produced; and though there was some difficulty in conducting the process, in one experiment which they made, they succeeded so far, that ten grammes of charcoal disappeared. The liquid, in its combustion, gives a smell of sulphurous acid, deposites sulphur, and leaves a residuum of charcoal. From these results, they considered it as a compound of sulphur and charcoal, and gave it the name of Carburetted Sulphur †.

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* Philosophical Magazine, vol. xx. p. 131.

† Annales de Chimie, tom. xlii ; Philosophical Magazine, vol. xiii.

Amedée Berthollet undertook a series of experiments to determine the constitution of this substance. He employed the process of Clement and Desormes, that of passing sulphur over ignited charcoal in a tube. Gas was disengaged, accompanied with white vapours, which condensed into an oily-like fluid. To produce much of this fluid, it was necessary to keep the charcoal at a full red heat, and to pass over it only a slight excess of sulphur; if too little sulphur were employed, the product was chiefly a permanent gas; if too much were used, a solid substance was obtained of a crystalline appearance, the production of which had likewise been observed by Clement and Desormes. The gas was similar to sulphuretted hydrogen, except that it was less soluble in water. The liquid had all the properties of the substance described by Lampadius. To determine its composition, it was submitted to combustion; it was entirely consumed, without leaving any trace of charcoal, though, when imperfectly burnt, it gave a residuum of sulphur. In the elastic products of the combustion, no indication of carbonic acid could be found, lime water not being rendered milky, when the vapour of it mixed with oxygen was detonated over it. In decomposing it by the action of oxymuriatic acid, sulphur was deposited, but without any appearance either of charcoal or of carbonic acid; and in its evaporation there was a residue of sulphur without any trace of charcoal. Berthollet, from these results, inferred that it is a compound of sulphur and hydrogen; the hydrogen which forms it being derived both from the sulphur and charcoal [*].

Robiquet, assisted by Vauquelin, also made experiments on this substance, and could discover no indication of carbon in its composition [†].

Cluzel, from a long and complicated investigation of this subject, inferred that carbon, sulphur, hydrogen and

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[*] Mémoires d'Arcueil, t. i, p. 304.
[†] Philosophical Magazine, vol. xxx. p. 30.

nitrogen exist in the composition of this fluid, and that the sulphur is in some different state, different from that in which it is usually obtained, probably de-oxygenated, as it required a larger quantity of oxygen to convert it into sulphurous acid [*].

In a report on the memoir of Cluzel, by Berthollet, Thenard, and Vauquelin, experiments are given as executed by the latter chemist, which prove that this substance is composed entirely of sulphur and carbon. When transmitted slowly over ignited copper on a porcelain tube, it suffered complete decomposition ; and if a sufficient quantity of copper were employed, no gas whatever was produced ; the product was sulphuret of copper with charcoal ; the copper was dissolved by diluted nitrous acid, the sulphur was sublimed from the charcoal ; and from the results the composition was inferred to be 85 or 86 of sulphur with 15 or 14 of carbon [†].

Berzelius and Dr Marcet had about the same time undertaken a similar investigation. They ascertained that no hydrogen exists in the composition of this substance, its vapour detonated with oxygen gas, or the liquid itself transmitted over metallic oxides at a red heat affording no water, and oxymuriatic acid producing by its action on it no muriatic acid. The presence of carbon in it was demonstrated by its affording, when burnt in oxygen gas, alongst with sulphurous acid, carbonic acid and carbonic oxide gases ; and by carbonic acid being formed after it had remained mixed for some time with barytic water, lime water, or potash ley. The proportions of its elements were determined from its decomposition by passing it slowly through an ignited tube filled with red oxide of iron. Carbonic acid and sulphurous acid gases, and sul-

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[*] Annales de Chimie, tom. lxxxiv. ; Philosophical Magazine, vol. xliii.

[†] Annales de Chimie, tom. lxxxiii, p. 274.

phuret of iron were formed : the sulphuret of iron was dissolved in nitro-muriatic acid and the sulphur converted into sulphuric acid ; and thus, from the quantities of the three acids, the quantities of sulphur and carbon could be determined. The proportions found were nearly the same as those assigned by Vauquelin,—84.83 of sulphur and 15.17 of carbon *.

Carburetted sulphur, formed by transmitting sulphur slowly over well calcined charcoal at a red heat, is at its first production frequently of a yellow colour : but this is owing to an excess of sulphur. When purified by a second distillation with a gentle heat, it is colourless and transparent, its smell is disagreeable and pungent, its taste is at first cool, but soon becomes sharp and acrid ; its specific gravity, according to Lampadius and Clement, is 1300, according to Berzelius and Marcet 1272 ; it sinks therefore in water ; it is very volatile, evaporating rapidly at natural temperatures, and producing in its evaporation a great degree of cold ; its power in this respect is so great that Dr Marcet caused quicksilver to freeze by its evaporation ; the bulb of a thermometer covered with linen, and wetted with it, sinks in the air from 60° to 0 ; and in the receiver of an air-pump, on moderate exhaustion from 60 to —80 ; it passes entirely into vapour *in vacuo*, and it adds greatly to the volume of any elastic fluid ; under a common atmospheric pressure it boils at 105° ; it does not congeal at —60°.

It is inflammable, burns with a blue flame and without smoke, with the emission of copious fumes of sulphurous acid. Its vapour mixed with atmospheric air burns with a blue flame without detonation ; it detonates with oxygen gas.

Carburetted sulphur is not soluble in water ; it dissolves in alkohol and ether, and in oils ; it dissolves sulphur rea-

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* Philosophical Transactions, 1813.

dily, acquiring a yellow colour, and likewise phosphorus without the assistance of heat; but does not act on charcoal. It is scarcely acted on by the metals at a common temperature; quicksilver digested in it suffers no change, nor does its vapour affect lead, but at an elevated temperature several of them decompose it by attracting its sulphur; potassium, which does not act on it in the liquid state, inflames when heated in its vapour. It throws down precipitates from several of the metallic salts.

The acids scarcely act upon it: the sulphuric and muriatic produce no sensible effect; the nitric, when aided by heat, has been said to decompose it. The nitro-muriatic left in contact with it, for some weeks, converts it into a product having the appearance and several of the chemical properties of camphor. This Berzelius regards as a triple acid, composed of the sulphuric, muriatic and carbonic. It absorbs ammoniacal gas slowly, and forms a saline mass.

Carburetted sulphur has no acid property: it does not affect the colour of litmus; it combines however with alkaline bases. Ammoniacal gas exposed to it is slowly absorbed, and a solid compound is formed which sublimes unaltered in close vessels, and deliquesces rapidly on exposure to the air. When the vapour of the carburetted sulphur is passed over lime heated in a tube, it is absorbed, and a solid product is formed, tasteless and insoluble in water: with barytes and strontites the results are similar: all these compounds, when heated with water, suffer decomposition, and hydro-sulphurets are formed. Berzelius has named them Carbo-Sulphurets.

CHAP. IV.

OF PHOSPHORIC ACID, AND ITS BASE.

This acid, though it exists in the mineral kingdom, in combination with certain metals and earths, is more peculiarly a product of the animal system. Combined with lime it forms the basis of bone, and it exists also in several varieties of animal matter. It was discovered, not by being procured in its insulated form from any of these combinations, but in an indirect mode. It was known to some of the alchemists, that from certain animal products, a substance could be procured so highly inflammable as to burn on exposure to the air. This is the substance named Phosphorus. It was found to form an acid in burning, and it was discovered, that in the processes by which it had been obtained, it was always derived from the decomposition of this acid; and thus the existence of the acid and its relation to phosphorus were established. The base combines with a lower proportion of oxygen, forming Phosphorous Acid: and, according to recent investigations, with a still lower proportion forming what has been named Hypophosphorous Acid. It also unites with hydrogen and sulphur. We have, first, to consider the chemical properties of the base itself, and afterwards those of these compounds.

Sect. I.—*Of Phosphorus.*

This substance, the base of phosphoric acid, must have remained unknown but for the researches of chemistry. It combines spontaneously with oxygen, at the lowest natural temperature, and cannot therefore exist pure in nature, and there is even considerable difficulty in obtaining it from any of its combinations. It appears, from the enigmatical expressions of some of the earlier alchemists, that it was known to them. Brandt, however, an alchemist of the 15th century, is regarded as the proper discoverer of it. He kept secret the method of procuring it. Kunckel, another German chemist, informed of Brandt's discovery, and knowing that the phosphorus had been obtained from urine, entered on the investigation, and succeeded in discovering the process. It appears also to have been known to Boyle. Such however was the difficulty of preparing it, that it was attempted by few chemists. Subsequent researches have discovered methods of obtaining it with more facility, though the process is still somewhat complicated.

It is always procured by submitting phosphoric acid to heat with carbonaceous matter, which attracts its oxygen, and allows the phosphorus to be volatilized. This acid, though it exists in the mineral kingdom, occurs principally in certain varieties of animal matter, and it is from these that it is procured for the preparation of phosphorus.

It exists in considerable quantity in urine, in combination with ammonia, soda, and lime, and it was from this fluid that it was obtained by the earlier chemists. The essential steps of the process appear to have consisted in obtaining by evaporation these salts, mixed with the extractive matter of the urine. This was subjected to distillation in close earthen-ware retorts, capable of sustaining a very strong fire. The charcoal of the extractive matter attracts

the oxygen of the phosphoric acid, and a portion of phos-
phorus is volatilized by the strong heat applied.   A con-
siderable improvement was made in the process, by adding
a quantity of charcoal powder previous to the distillation,
by which the phosphoric acid was more completely decom-
posed.   Another improvement, made by Margraaf, con-
sisted in adding a portion of muriate of lead, by which the
product was increased, from the circumstance that the phos-
phoric acid combined with the soda and the lime is unit-
ed by too strong an affinity to these bases to admit of be-
ing decomposed by charcoal alone, with the same facility
that the acid combined with the ammonia suffers this de-
composition: but the muriate of lead decomposes the phos-
phates of soda and lime, by attracting the phosphoric acid,
and thus facilitates its decomposition by the charcoal.

Still the process was offensive and laborious.   Scheele,
by discovering that phosphoric acid exists in bone, gave
one less so, and which, with some variations, is now fol-
lowed in the preparation of phosphorus.

Bones are burnt to whiteness in an open fire.   This
white matter, of an earthy-like appearance, consists prin-
cipally of phosphate of lime.   It is reduced to a coarse
powder, is diffused in ten times its weight of water, and a
little more than half its weight of sulphuric acid (4 parts to
6) is added to it in an earthen vessel ; the mixture is kept
in a moderate heat, for 12 or 24 hours, stirring it occa-
sionally, and adding water, as may be necessary, to pre-
serve it soft.   It is then placed on a filtre of cloth, and
boiling water is poured upon it, until, in filtrating through
the mass, it ceases to acquire acidity.

The acidulous liquor thus procured was supposed to be
phosphoric acid, separated from its combination with the
lime, by the superior affinity of the sulphuric acid; it is,
however, a solution of super-phosphate of lime, the sul-
phuric acid acting partially on the phosphate of lime of
the calcined bone, and abstracting a portion of its lime ;

while a portion remains combined with the phosphoric acid. The sulphate of lime is comparatively insoluble; the superphosphate of lime is more soluble, and by washing with water it is separated from the undissolved matter.

In the farther steps of the process, the acidulous liquor is evaporated (according to Pelletier's recommendation, in a bason of copper) to dryness, and the dry mass is even fused by the application of heat. To this solid matter, reduced to powder, is added half its weight of charcoal powder, and the mixture is put into a coated earthen retort placed in a naked fire, and having a long tube adapted to it, which terminates in a vessel of water, the extremity being immersed a little in the water; the heat is raised sufficiently to enable the charcoal to attract the oxygen of the phosphoric acid, and to distil over the phosphorus, which condenses in part in the tube, and is partly received in the water. The quantity obtained varies according as the operation is skilfully conducted. Pelletier states, that by one distillation he had often obtained 60 ounces of phosphorus, 30 pounds of sulphuric acid, and 36 pounds of calcined bones having been used *, and at other times not more than 30 ounces.

A loss however is sustained in consequence of the lime, by its affinity to the phosphoric acid, preventing a portion of it (not less, according to Vauquelin, than one half of the quantity present) from being decomposed by the charcoal. To obviate this, Vauquelin adopted an improvement, suggested by Margraaf, adding to the superphosphate a quantity of acetate, (or, what is preferable, nitrate of lead); the oxide of lead combines with the phosphoric acid, and forms an insoluble precipitate; this phosphate of lead is washed with water, dried, mixed with half its weight of charcoal, and exposed to heat as in the preceding process. But although in this way the whole of the phosphoric acid,

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* Mémoires de Chimie. tom. ii, p. 252, 284.

or nearly the whole, is decomposed by the charcoal, there is a loss of phosphorus by the combination it forms with the lead, reduced to the metallic state. This has been proposed to be remedied, by decomposing the phosphate of lead by muriatic or sulphuric acid; but this renders the process more complicated. The best method appears to be that pointed out by Dr Higgins *,—adding to the super-phosphate of lime, obtained from the decomposition of the burnt bones, carbonate of ammonia, so as to produce neutralization. The carbonic acid combining with the lime, the phosphoric acid is united with the ammonia; this phosphate of ammonia remains dissolved; the solution is poured off, is evaporated to dryness, and is urged with a red heat in a thin glass vessel; the ammonia is expelled, the phosphoric acid, nearly pure, remains in a vitrified state; it is reduced to powder, mixed with half its weight of charcoal, and submitted to distillation in the usual mode. This process has the advantage, too, that the phosphorus is obtained purer, and in particular free from any sulphur, with which, in the other modes, it is liable to be contaminated, from part of the sulphuric acid employed in the decomposition of the burnt bones being retained in the subsequent steps; while in this it is expelled in combination with the ammonia, from the phosphoric acid.

The distillation of the phosphorus, according to any of these methods, requires considerable care. The principal circumstances have been pointed out by Dr Higgins. Earthen retorts are in general so porous at a high temperature, that a great part of the phosphorus is lost; the retort, therefore, ought to be previously washed externally with a strong solution of two parts of borax mixed with one of lime, which during the incandescence forms a glazing that renders it impervious. By being farther coated with clay and sand, it is less liable to injury from any sud-

* Minutes of a Philosophical Society.

den alteration of temperature. The retort should have a wide neck, and the tube connected with it, which dips a little in water, should be equally wide, that the phosphorus, in distilling over, may not, by congealing, so far close the aperture as to prevent the escape of the elastic fluid, consisting of carbonic oxide and acid holding a little phosphorus dissolved, which is disengaged. When from the diminution in the size of the bubbles of air which escape, there is reason to fear this, a hot iron ought to be applied to the tube to melt any phosphorus. A portion of the gas disengaged during the distillation ought to be collected and introduced into the neck of the retort as it cools at the end, to prevent the water from passing back, as atmospheric air admitted for that purpose would kindle the film of warm phosphorus in the tube.

Phosphorus obtained by the first distillation is opaque and of a dark brown colour, from the presence of carbonaceous matter. Different methods are practised to purify it. Distillation succeeds, though it is somewhat difficult, from the risk of the first portion of phosphoric vapour taking fire from the action of the air of the retort : this may be obviated by filling the retort with hydrogen gas, before proceeding to distillation ; it is then placed in sand, the extremity of the neck remaining immersed in water ; the phosphorus, by the application of heat, is distilled over, and is obtained colourless and transparent *. Another method is to digest the phosphorus with nitrous acid, or, as Moussin Poushkin recommended, with nitromuriatic, or oxymuriatic acid †; which renders it colourless by oxidating the carbonaceous matter. According to Pelletier, however, the nitrous acid (and the oxymuriatic will have probably the same effect) oxidates a portion of the phosphorus, and renders it less inflammable.

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* Minutes of a Society for Philosophical Exper. p. 261.
† Annales de Chimie, tom. xxv, p. 102.

The simplest method, suggested by Woulfe, and recommended by Pelletier, is straining through fine chamoy leather. The impure phosphorus is put into a piece of leather of this kind, tying it in the form of a bag, and covering it with cold water: the water is heated until the phosphorus is melted; it is then pressed through the leather, taking care to keep it always under the water; it is thus obtained pure, while there remains on the leather a quantity of red-coloured matter, which Proust and others have affirmed to be a compound of phosphorus and charcoal. It has been affirmed by Stienacher, that the phosphorus purified in any of these ways still retains a little carbon, as, when kept in fusion, it deposites a little of this red matter, or, if kindled, leaves a red trace. It is not very clear, however, that this substance is a carburet of phosphorus, and the quantity of it is inconsiderable.

Phosphorus is generally run into cylindrical pieces, by placing it in small funnels with cylindrical necks or tubes, closed at the extremity with a cork, and placed in a perpendicular position under water, which is gradually heated so as to melt the phosphorus; it sinks into the tube of the funnel; as the water cools, the phosphorus becomes concrete, and when cold is pushed out by the wide end of the tube.

Phosphorus was regarded as a simple substance. Sir H. Davy supposed that it contained hydrogen, from finding that in submitting it to galvanic action a portion of phosphuretted hydrogen is evolved. He farther inferred that it also contains a small proportion of oxygen, from finding, that when combined with potassium, the power of the potassium in decomposing water appeared to be diminished, so that it afforded less hydrogen, indicating that oxygen had been previously communicated to it [*]. These results were shewn to be incorrect. Gay-Lussac and

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[*] Philosophical Transactions, 1809.

Thenard found, that in the combination of phosphorus and potassium there is no sensible disengagement of gas; they conclude, therefore, that there are no grounds whence it can be inferred that phosphorus contains hydrogen; and in the production of phosphuretted hydrogen gas by the action of phosphuret of potassium on water, there is no deficiency observed, whence it can be inferred that phosphorus contains oxygen *. Phosphorus must therefore, in the present state of our knowledge, be regarded as a simple substance.

Phosphorus, when purified, is nearly colourless, or of a white colour, and semi-transparent. Frequently it has a grey or yellowish tinge, probably from impurity. It becomes red, according to Vogel, when exposed to solar light, and this whether it is exposed in a vacuum in nitrogen or hydrogen gas, or under water deprived of air †. It has a consistence and tenacity similar to wax; it is rather harder, but can be easily cut by a knife. Its fracture often presents a radiated appearance. Its specific gravity is 1.714.

According to the observation of Pelletier, it is capable of crystallizing. When fused under water, on becoming concrete, if the external crust be pierced and the liquid withdrawn, a crystallization in needles, like that of sulphur, or in octohaedrons if the cooling has been slow, is obtained. It also crystallizes from its solution in an essential oil ‡. Its melting point is about 99 of Fahrenheit, though this varies in different specimens, owing, as Pelletier supposed, to the presence of sulphur. At 219 it is volatilized; at 554 it boils in close vessels §.

When phosphorus is exposed to atmospheric air, it emits fumes which have somewhat of a fœtid smell: in a dark

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* Recherches Physico-Chimiques, tom. i, p. 208, 210.
† Annales de Chimie, t. lxxxv, p. 225.
‡ Mémoires de Chimie de Pelletier, 1. 256. § Ibid. p. 290.

place, the phosphorus is luminous, and it is suffering a
real combustion. This is so slow. that it is not percepti-
ble in day light, by the emission of light, and so little ca-
loric is extricated that it can be held in the hand. At a
higher temperature, as that of 100, the combustion is
more vivid; and at 160 it burns with a bright flame, with
much heat, and with the copious production of white va-
pours. The combustibility of phosphorus is much increas-
ed by its minute division, or by friction, so that, if rubbed
slightly, the heat of the hand is sufficient to inflame it;
and from this circumstance accidents have often happen-
ed, in making experiments with it incautiously.

The combustion of phosphorus is applied to the purpose
of Eudiometry. When the rapid combustion excited over
mercury by the application of heat is employed, the re-
sult is sooner obtained, but it is inconvenient, as some
contrivance is necessary to prevent part of the air from
being forced out of the vessel, and as the combustion ceases
before the whole of the oxygen is consumed, so that it
is necessary after all to leave the phosphorus in contact
with the air for some hours. The method by slow com-
bustion is therefore preferred.

Gren applied the phosphorus to this purpose, by pla-
cing at the orifice of a graduated tube, filled with the air
designed to be submitted to trial, and surrounded with
water, a small bit of phosphorus fixed on a cork to which
a thread was attached. As the oxygen of the included
air was absorbed, the cork rose on the water within the
tube. When the process appeared to be finished, it could
be withdrawn by the thread. This, however, proceeds
slowly, and the method of Berthollet, in which a larger
surface of phosphorus is presented to the air, is preferable.
A tube divided into 100 parts is filled with the air design-
ed to be tried, and this air is transferred into another tube,
somewhat larger, previously filled with water; a cylindri-
cal piece of phosphorus is fixed on a glass rod, which is

introduced into the vessel containing the air, so as to be
exposed to it. The oxygen is gradually abstracted by the
phosphorus. When the abstraction is complete, which is
known by the disappearance of any whitish vapours, or
any luminous appearance, the remaining air is transferred
into the tube in which it was first measured, and the di-
minution of volume it has suffered is ascertained. The
experiment is generally finished in from 2 to 6 or 8 hours,
according to the quantity of the air, and the size of the
stick of phosphorus.

There is one correction to be made, to render the re-
sult accurate. The diminution of volume which atmo-
spheric air sustains from exposure to phosphorus is less
than that from other eudiometrical methods; and this has
been found to be owing to a little of the phosphorus being
dissolved in the residual nitrogen gas, and augmenting its
volume. This augmentation of volume, Berthollet states
to amount to about a fortieth of the nitrogen gas. The
diminution of volume produced by the phosphorus in at-
mospheric air is about 20 in 100; leaving, of course, 80
of nitrogen. But, according to this correction, a fortieth
of this (or 2 parts) is to be added, to make the real dimi-
nution, and this gives 22 in 100. The method is simple
and easy, and it has the important advantage of indica-
ting when the process is finished; for while any oxygen
remains in the air, the phosphorus is surrounded with a
white vapour, observable in day light, and in a dark place
it appears luminous. When the oxygen is entirely ab-
stracted, these appearances cease, and the air around the
phosphorus is transparent. It has been stated as a source
of error by Thenard, that a little carbonic acid is formed
from the oxygenation of the carbon often present in phos-
phorus; but according to the experiments of Vogel, no
perceptible quantity can be discovered.

The phenomena exhibited by the combustion of phos-
phorus in oxygen gas at an elevated temperature, are such

as might be expected compared with those which it presents in atmospheric air   The illumination is extremely vivid, and there is the evolution of much heat.

A singular fact connected with the combination of phosphorus with oxygen is, that although in atmospheric air it suffers a slow combustion at low temperatures, as at 50 or 40 of Fahrenheit, it does not do so in pure oxygen gas.   When a piece of phosphorus is placed in perfectly pure oxygen, no luminous appearance can be discovered even in the dark, at a temperature at which it would be luminous in atmospheric air, and it does not suffer any evident change.   It requires to be heated to 80° to shine, and to 104 to burn vividly.

This fact seems first to have been attended to by Göettling, a German chemist.   He had observed, that phosphorus appeared luminous in nitrogen gas, and that it is changed into an acid ; while in oxygen gas the appearance of combustion is more faint, and at length ceases ; and from these observations he drew conclusions unfavourable to the antiphlogistic theory.   The subject soon engaged the attention of chemists, and the facts with regard to it were ascertained.   It has been shewn, that the luminous appearance of phosphorus in nitrogen gas is faint, and continues only for a short time ; that if, after it has ceased, a little oxygen be admitted, the whole gas becomes immediately luminous.   In a certain time this ceases, from the consumption of the oxygen ; but if a fresh quantity be admitted, the luminous appearance is again produced.   If the nitrogen be perfectly free from oxygen, the phosphorus exhibits in it no luminous appearance even in the dark ; but if a little of it is added to oxygen gas, a corruscation of light immediately occurs.

These phenomena appear to depend on the solubility of phosphorus in nitrogen gas.   It was proved by the experiments of Vauquelin, that it is dissolved in small quantity by this gas, and that, when presented in this state to oxy-

gen, the phosphorus and oxygen combine; hence the spon-
taneous combustion in atmospheric air. But, without this
previous solution, a higher temperature is necessary, and
hence the reason why phosphorus requires to be heated,
to burn in oxygen gas. The luminous appearance which
it exhibits in nitrogen gas is owing to the gas not being
pure, but containing a little oxygen, to which the dissolv-
ed phosphorus is presented, and its shining in oxygen gas
is owing to a similar impurity from the admixture of ni-
trogen. From the experiments of Vauquelin and Brug-
natelli it appears that hydrogen acts on phosphorus in a
similar manner with nitrogen. A piece of phosphorus
immersed in pure hydrogen does not produce light, but
when, after a few hours, the gas which has been thus ex-
posed is transmitted into a jar of oxygen gas, a vivid light
is perceived. Nay, what is singular, it is proved that phos-
phorus is soluble in oxygen gas, without the phenomena
of combustion being presented during the solution, while
the luminous appearance is produced by the addition of
nitrogen or hydrogen. This Vauquelin and Fourcroy
established, by exposing phosphorus to pure oxygen gas
for some hours; it had not in that time emitted any light,
but on introducing to it nitrogen gas, a blue lambent light
was immediately perceived. They endeavour to account
for it, but perhaps not very satisfactorily, by the hypothe-
sis, that in the simple solution of phosphorus by oxygen
gas, there is no intimate combination, no decomposition
of the gas and separation of its light and caloric; and that
when nitrogen or hydrogen gas is added to the solution,
it produces a separation of the particles of the phosphorus,
a diminution, therefore, of their cohesion, and hence has
the same effect as a slight elevation of temperature, which
is capable of causing phosphorus to burn in oxygen [*].

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[*] Annales de Chimie, tom. xxi. p. 189. Ibid. tom. xxii,
p. 246. Nicholson's Journal, 4to, vol. i, p. 444, and ii, p. 8.

Fourcroy and Vauquelin found, that phosphorus does not become luminous in carbonic, sulphurous, muriatic, or fluoric acid gas, or in ammonia ; nor did any of these gases, after they had been exposed to it, produce any luminous appearance on the addition of oxygen. In nitric oxide gas, if introduced in a state of combustion, it continues to burn, and with nearly as much splendour as in oxygen gas. In oxymuriatic gas it melts, and, when the temperature is above 70 or 80 of Fahrenheit, burns with brilliant sparks, and with the production of copious white fumes. It exhibits a similar appearance in nitrous acid vapour. If a few small pieces of phosphorus be put into nitrous acid, the acid suffers decomposition by the phosphorus attracting oxygen, and very dense red coloured vapours are disengaged. If, by the violence of the effervescence, any pieces of phosphorus are buoyed up into this vapour, a flash of light is perceptible.

Phosphorus combines with oxygen in different proportions, forming different compounds : with the largest proportion the result is an acid, inodorous, concrete, and fixed ; with a less proportion of oxygen another acid is formed slightly fœtid, somewhat volatile, and when heated exhaling a vapour which appears luminous in the dark. The former has been named Phosphoric, the latter Phosphorous Acid. The existence of an Oxide of Phosphorus has also been supposed. The reddish matter with which phosphorus is usually covered, or which it leaves as a residuum, when the combustion of it has been incomplete, or has been suddenly checked, and which is highly inflammable, has been considered as an oxide ; but this is not proved by any conclusive experiment. Proust, Thenard, and others, have considered it as a carburet of phosphorus. Vogel appears to have shewn that it contains no sensible quantity of carbon, and has revived the opinion that it is an oxide, but without any sufficient evidence [*]. Stein-

* Annales de Chimie, tom. lxxxv, p. 248.

acher affirmed, that the white vapour, which is sublimed when phosphorus is heated in a long and slender glass tube, and which condenses into a flocculent matter not acid, but capable of attracting humidity, and passing by exposure to the air into phosphorous acid, is an oxide at the minimum of oxidation, and that another white oxide exists which forms on the surface of phosphorus, when it is kept immersed in water, and is also obtained by the action of liquid oxymuriatic acid *. The existence of these oxides is, however, problematical, and the two acids were, until lately, the only well defined compounds of phosphorus with oxygen.

Lavoisier had inferred, that 100 of phosphorus combine in burning with 154 of oxygen, forming 254 of phosphoric acid. Rose, by oxygenating phosphorus by nitric acid, obtained as the proportion 100 with 114 of oxygen; and Berthier, from the same method, assigned that of 100 with 122. Sir H. Davy, from the direct combustion of phosphorus in an excess of oxygen gas, obtained a result very similar to that by Lavoisier, 100 of phosphorus combining with 153 of oxygen †; while Dr Thomson, by the same method, obtained the proportion of 100 with 123.46 ‡. The composition of phosphorus acid has been assigned with nearly as much discordance. By Thenard it was stated at 100 of phosphorus with 110.4 of oxygen §, by Sir H. Davy at 100 with 75, and by Dr Thomson at 100 with 66.6.

More recent investigations have given other views on this subject, but have scarcely established more certain results. Berzelius endeavoured to discover the quantity of oxygen in phosphoric acid, by reducing certain metallic

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* Nicholson's Journal, 8vo, vol. vi, p. 133.
† Philosophical Transactions, 1812.
‡ Annals of Philosophy, vol. vii, p. 305.
§ Annales de Chimie, t. lxxxv, p. 326.

solutions, those, in particular, of gold and silver, by phos-
phorus, and comparing the quantity of phosphorus oxy-
genated with that of metal reduced : the proportions he as-
signed are 100 of phosphorus with 128.17 of oxygen. The
proportions in phosphorus acid he inferred from the de-
composition of the product formed by the action of oxy-
muriatic acid on phosphorus in excess, and which, accord-
ing to the view he supports, consists of this acid com-
bined with the muriatic ; the result gave 100 of phospho-
rus with 76.92 of oxygen, coinciding nearly with the pre-
vious determination by Davy *.   The ratio of oxygen in
the two acids, according to these proportions, is that of
3, 5.   Davy had inferred, conformable to the common law
of multiples, that it is that of 1, 2; and Gay-Lussac had
supposed it to be 2, 3. The results of Berzelius, however,
independent of the difficulties attending his modes of ana-
lysis, do not appear to correspond with the equivalent
combining quantities of these acids as inferred from their
salts ; and the peculiar relation in the two proportions
lead to the conclusion, that other combinations exist.

Dulong has maintained the existence of not less than
four acids having phosphorus for their base. The first, to
which he has given the name of Hypophosphorous Acid,
and which had not been before observed, is obtained by the
action of water on an alkaline phosphuret ; it consists of
100 of phosphorus with 37.44 of oxygen. The second is
the Phosphorous acid, formed by the process originally
given by Davy of decomposing the chloride of phosphorus
by water ; its composition is 100 of phosphorus with 74.88
of oxygen, almost precisely the same with that which Davy
had assigned. The name of Phosphorous Acid had been
given to the compound formed by the slow combustion of
phosphorus in atmospheric air.   It had been consider-
ed as having usually an intermixture of phosphoric acid.

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* Annales de Chimie et Physique, tom. ii, p. 217.

Dulong finds, however, that the proportion of oxygen in it is always the same, and it therefore is to be regarded either as a definite compound of phosphorus and oxygen, which by the action of salifiable bases is resolved into these two acids, or as a definite compound of these acids. He is inclined to adopt the latter opinion. He gives it the name of Phosphatic acid. It is this acid which had been analysed by Thenard, under the name of Phosphorous acid, the composition of which he stated at 100 of phosphorus with 110.4 of oxygen. Dulong assigns as the proportion 100 with 109. There is, lastly, the Phosphoric acid; this he finds to be composed of 100 of phosphorus with 124.8 of oxygen *.

In these four acids the oxygen in the two first is in the ratio of 1, 2, in the third the proportion would require to be 112.3 instead of 109 to give the multiple 3, and this is a deviation not greater than what may fall within the limits from errors of experiment. In the fourth it deviates altogether from the multiple 4; it is much less, being to that of the second compound in the ratio of 5 to 3. Phosphoric acid, however, as analysed in these experiments, does not exist insulated; it contains, according to the common expression of the fact, combined water. If, according to the view I have stated with regard to acidity, this water be considered as existing in the state of its elements, and if the proportion of it essential to the constitution of the ternary acid were accurately determined, its oxygen might give the multiple 4, and establish the regular progression.

Still another view has been given of these combinations. Dr Thomson inferred the composition of phosphorous and phosphoric acids, from the analysis of phosphuretted hydrogen by oxygenation; and correcting Dulong's results by those obtained by this method, he assigns as the pro-

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* Annales de Chimie et Physique, t. ii, p. 141.; Philosophical Magazine, vol. xlviii.

portions,—in hypophosphorous acid 100 of phosphorus
with 33.3 of oxygen, in phosphorous acid 100 with 66.6,
and in phosphoric acid 100 with 133.3 *. Sir H. Davy
has, from a different mode of investigation, given precisely
the same proportions. The phosphatic acid of Dulong he
does not admit as a definite compound †. The propor-
tions thus assigned give the oxygen in the different com-
pounds in the ratio of 1, 2, 4. The relation of water, or its
elements, to the composition in all, or any of them, is, how-
ever, still undetermined ; it may supply the intermediate
multiple. And as phosphoric acid exists with a definite
proportion of combined water, according to the common
expression of the fact, which cannot be abstracted from it,
there must be an acid of ternary composition, or hydro-
phosphoric acid, having a higher proportion of oxygen.
The whole subject, therefore, evidently remains for far-
ther investigation.

The details with regard to the composition of these dif-
ferent compounds will be given under their individual his-
tory.

Phosphorus combines with hydrogen in two propor-
tions. Both compounds are gaseous : it also unites with
sulphur. These combinations form subjects of a separate
section.

Phosphorus has been supposed to combine with carbon.
According to Proust the combination is effected when phos-
phoric acid is decomposed by charcoal at a red heat, in the
common process of obtaining phosphorus ; and it consti-
tutes the red matter, which, being less fusible than phos-
phorus, remains, when the phosphorus is melted, under wa-
ter, and strained through leather. If it be distilled, it yields
any phosphorus it contains in excess ; but the real com-
bination is not subverted, unless the degree of heat be much

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* Annals of Philosophy, vol. viii, p. 91. ; vol. ix. p. 36.
† Ibid. vol. xi, p. 382.

raised. When it reaches ignition, a fresh quantity of phosphorus is sublimed, and the residue is charcoal. It burns easily when heated, but by exposure to the air becomes less inflammable *. This combination, however, of phosphorus and carbon is doubtful. Vogel, as has been already remarked, was unable to discover any carbon in this red coloured matter. Dr Thomson has stated, that a carburet of phosphorus is obtained when phosphuret of lime is dissolved in muriatic acid. He describes it as a tasteless substance of a lemon yellow colour, which does not melt when heated, but burns with considerable splendour, and which attracts moisture from the air †.

Phosphorus unites with many of the metals, forming compounds, to be afterwards described.

With the alkalis and alkaline earths, phosphorus combines when their action is favoured by heat, as by passing it in vapour over the ignited alkali or earth in a tube. These compounds are of a dark colour. Their chemical relations can scarcely be examined, as they rapidly decompose water, and are decomposed by it, phosphuretted hydrogen being formed. Their history is to be afterwards given.

Phosphorus is soluble in a number of inflammable liquids, such as oils expressed or volatile, alkohol, or ether, and forms fluids, which, by agitation with atmospheric air, or decomposition by water, produce illumination. The solution in expressed oil is prepared by putting two or three small pieces of phosphorus into a flask, pouring upon them olive oil, and applying heat by a sand bath, until the phosphorus is dissolved. On rubbing the hand with this oil, it appears luminous in the dark, without being accompanied with any sensible emission of heat. The solution of phosphorus can also be effected in the essential oils, as those of lavender of turpentine, though, from their

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* Nicholson's Journal, 4to, vol. iv, p. 355.
† Annals of Philosophy, vol. ix, p. 28.

volatility, more care is requisite in applying heat. These are less luminous when agitated with the air. Mr Accum has observed, that the phosphuret of sulphur is also soluble in oils, and that this forms a liquid more luminous when exposed to the air than the solution of phosphorus alone. It dissolves by rubbing with the oil, and no heat ought to be applied, as it gives rise to explosion.

Alkohol is capable of dissolving phosphorus, a little of it being put with the alkohol into a strong phial well corked, and heat being moderately applied. Very little is dissolved, but the alkohol acquires a perceptible odour, and if a little of this phosphuretted alkohol be dropt on water, a flash of light is disengaged from the surface, which appears vivid in a dark place; or a feather dipt into water and immersed in the solution produces a luminous appearance. Sulphuric ether dissolves phosphorus; but the solution does not give light when mixed with water. Both solutions are decomposed by water, and phosphorus is precipitated. The phosphuretted alkohol Grotthus has shewn decomposes the greater number of metallic salts, and throws down from their solutions dark coloured precipitates, which are phosphurets either of the metals or their oxides.

SECT. II.—*Of Phosphoric Acid.*

PHOSPHORIC ACID is formed in the rapid combustion of phosphorus, either in atmospheric air or in oxygen gas. When the experiment is performed over mercury, it is obtained in the form of a white flocculent matter, which is deliquescent, so as to become liquid on exposure to the air.

The proportions of phosphorus and oxygen in the composition of phosphoric acid, it has been stated in the preceding section, have been assigned with much diversity on different authorities. Of the earlier experiments, those of Lavoisier, on the direct combustion of phosphorus, gave 100 of phosphorus with 154 of oxygen; those of Rose, on its oxygenation by nitric acid, gave 100 with 114; those of Berthier, by the same process, 100 with 112; those of Davy, by the method of Lavoisier, a result very nearly the same as his, that of 100 with 153; and those of Dr Thomson, by the same method, 100 with 123.5.

In the more recent investigation of this subject, the method employed by Berzelius to determine the composition of the acid, was to digest a given weight of phosphorus with a solution of muriate of gold; a portion of the gold was reduced to the metallic state; the composition of oxide of gold being known, the weight of gold obtained gave the quantity of oxygen which had been transferred to the phosphorus; and the quantity of phosphorus necessary to effect the reduction being found, the composition of the acid might be inferred. The result was confirmed by a similar experiment with sulphate of silver. The proportions he obtained were 100 of phosphorus with 128.17 of oxygen, or 43.823 with 56.177 *.

Dulong, to determine the composition of phosphoric acid, submitted a metallic phosphuret, phosphuret of copper in particular, to the agency of nitric acid; sources of fallacy being avoided in this method which attend the direct action of nitric acid on phosphorus; and from the quantity of phosphoric acid produced, compared with the quantity of phosphorus oxygenated, the proportions could be inferred. And the results in this mode were confirmed by those obtained by converting phosphorus into phosphoric acid by the action of oxymuriatic acid with the

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* Annales de Physique et Chimie, tom. ii. p. 221—2.

contact of water, ascertaining the quantity of oxymuriatic acid necessary to produce the effect. From these methods he concluded, that 100 of phosphorus are combined with 124.8 of oxygen, or 44.48 with 55 52 *.

Dr Thomson has inferred the composition of phosphoric acid, from its production by the oxygenation of phosphuretted hydrogen. This gas is completely consumed when mixed either with one volume, or with one and a half of oxygen gas, phosphorus acid and water being formed in the first case, phosphoric acid and water in the second. The composition of phosphuretted hydrogen being known, and the quantity of oxygen spent in its conversion into water and phosphoric acid being thus ascertained, the composition of the acid may be determined. The result gives 100 of phosphorus with 133.3 of oxygen, or 42.86 with 57.11 †.

Sir H. Davy has lastly determined the composition of this acid by the direct experiment of the combustion of phosphorus; but to obviate the sources of fallacy which attend the common method of conducting this, he has employed the arrangement of burning the vapour of phosphorus as it issues from a small tube in oxygen gas. The result he has obtained is the proportion of 100 of phosphorus with 134.5 of oxygen ‡.

It remains to be determined by subsequent investigation, which of these estimates of the composition of phosphoric acid is just.

From the product of the combustion of phosphorus in oxygen, it is evident that a binary compound of these elements in proportions approximating to those now stated can be formed. It appears in the state of a white spongy

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* Annales de Physique et Chimie, t. ii, p. 148. Annals of Philosophy, vol. xi, p. 138.

† Annals of Philosophy, vol. viii, p. 91.

‡ Ibid. vol. xi, p. 328.

powder perfectly dry. But its chemical properties can scarcely be determined; for to admit of any examination of it, water must be present, and in this case an intimate combination is established with the water, or rather probably with its elements, and hydro-phosphoric acid is formed.

The substance formed by the combustion of phosphorus in dry oxygen gas absorbs water with great avidity, and with a hissing noise from the degree of heat produced. If exposed to the air it speedily deliquesces, and forms a dense oily like fluid. When this is exposed to heat, a portion of water is evaporated, the liquid becomes thick, and at length solid; and by exposing the dry matter to a full red heat, it is fused into a perfect glass, transparent, or with a slight opacity. By continuing or raising the heat it may be volatilized.

The acid in this state was supposed to be free from water; but it was found in various cases of its combinations with bases, that a considerable quantity of water is produced: the proportion has been variously estimated. By Berthier it was stated so high as 40 per cent. But this large quantity is probably not essential to the constitution of the acid. The quantity was stated by Berthollet to amount to a fourth of the weight of the vitrified acid. Dulong has assigned that of one-fifth nearly, or 20.6 in 100 parts *. This water cannot be abstracted by any other mode than that of the action of the acid on a salifiable base; the application of heat alone volatilizing the entire product without separation. This circumstance gives probability to the view, that the elements of water, not water itself, exist in the constitution of the acid. To no other acid can the same intensity of heat be applied; and if water were merely retained in it by an attraction exerted towards it, it

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* Journal des Mines, NO. 132. Mémoires d'Arcueil, t. ii, p. 64. Annales de Chimie et Physique, tom. ii, p. 149.

might be expected, considering the degree of attraction
which water usually exerts, that it would by so high a
heat be expelled.   But if the elements of the water exist
in combination with the base, this conclusion does not
follow; and even at the utmost intensity of heat, the con-
stitution of the acid as a ternary compound of phosphorus,
oxygen and hydrogen may be preserved.

Hydrophosphoric acid is more easily and more eco-
nomically obtained by other methods than by the direct
combustion of phosphorus, and various indirect processes
are usually employed.

It was once supposed that it may be obtained by the
process already described of decomposing the phosphate
of lime of calcined bone by sulphuric acid; but the liquor
obtained in this way, it has been stated, is a superphos-
phate of lime.   A marked difference was accordingly al-
ways observed between it and pure phosphoric acid.   The
latter, when fused, forms a species of glass, but is still ea-
sily soluble in water, and is even deliquescent, while the
glass obtained by evaporating the acid obtained from the
action of sulphuric acid on burnt bone, and fusing it, is
not deliquescent, and is very sparingly soluble in water, a
difference owing to the presence of the portion of lime.

Some method therefore must be followed to abstract the
lime.   Several have been proposed, but perhaps none can
be altogether relied on.   By carbonate of ammonia, the
greater part of the lime is thrown down in the state of car-
bonate of lime : and this process has been recommended
by Bouvoison,— carbonate of ammonia being added to the
superphosphate of lime to the point of neutralization, the
phosphate of ammonia being obtained by evaporation and
crystallization and then being exposed to heat in a silver
bason, so as to expel the ammonia.   Berthollet observes,
however, that the phosphate retains a portion of lime,
which is rendered evident, by adding to its solution car-
bonate of soda ; and although the acid thus obtained is de-

liquescent and soluble, it is not perfectly pure. According to Dulong, too, the whole of the ammonia cannot be expelled. Gay-Lussac has proposed to abstract the lime, by adding to the phosphoric acid concentrated by evaporation, oxalic acid, which unites with the lime, forming an insoluble precipitate; alkohol is added, which dissolves the pure phosphoric acid, and by evaporation this may be procured : but this process is expensive, and Berthollet maintains that a little lime still remains combined with the acid *.

It is therefore necessary, to be certain of having the acid pure, to obtain it by the oxygenation of phosphorus. It is not easy to do so by combustion, except on a small quantity. The method Pelletier employed was to transmit a current of air through phosphorus in fusion under water kept near to a boiling heat †. Lavoisier employed nitric acid, throwing into it, heated a little on a sand bath, small pieces of phosphorus, as long as any decomposition of the acid took place, raising the heat to assist the mutual action, as it became weak, and urging it with a strong heat at the end of the process, to expel any undecomposed nitric acid ‡. The process given by Fourcroy, which is more economical, and more easily conducted than any other, consists in adding to the phosphorous acid obtained by slow combustion, one-eighth of its weight of nitric acid of the specific gravity 1.3, and applying a gentle heat ; the excess of phosphorus in the phosphorous acid receives oxygen from the nitric acid, and the product is pure phosphoric acid. It ought to be evaporated and fused in a silver or platina cup, as it acts on earthen vessels and on glass.

The vitreous hydrophosphoric acid is abundantly so-

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* Chemical Statics, p. 429.

† Mémoires de Chimie, tom. i, p. 256.

‡ Journal de Physique, 1785, p. 1.

luble in water. It deliquesces on exposure to the atmosphere, and forms a dense colourless liquid. Its solution, even when much diluted, has a very sour taste, and immediately reddens the vegetable colours. It also exerts strong affinities to the alkalis and earths. It does not, however, exert much action on the metals, or on inflammable substances, apparently from the strong affinity with which its base retains oxygen. Sulphur produces no change on it, even with the assistance of heat. Charcoal decomposes it at a high temperature. If heated in its concrete state with those metals which have a strong attraction to oxygen, one portion of the metal attracts its oxygen, and another portion combines with the phosphorus, and produces a phosphuret; and its solution oxidates slowly those metals which can decompose water.

Phosphoric acid combines with the alkalis and earths, forming salts named Phosphates. The alkaline phosphates are soluble and crystallizable; they are also fusible, forming a kind of glass, and facilitate the fusion of a number of other substances. They are decomposed partially, in the humid way, by sulphuric and some of the other acids; in the dry way, and at a high temperature, these decompositions do not happen ; the phosphoric acid, on the contrary, from its fixity, being able to dislodge the more volatile acids. Phosphate of ammonia is decomposed by ignited charcoal, and phosphorus produced. Phosphates of potash, soda and lime, have usually been said not to suffer this decomposition, the affinity of these bases to the acid counteracting the affinity of the charcoal to its oxygen ; but according to some experiments by T. Saussure, all these phosphates are decomposed, requiring only a much higher heat to be applied: those of potash and soda are decomposed completely ; that of lime only partially, and by a very intense heat. Saussure remarks from this, that there is no vegetable or animal substance from which phosphorus may not be procured by an intense heat,

as there is none which does not afford alkaline or earthy phosphates by calcination *. The composition of these salts may be determined by precipitation by muriate of barytes; the phosphate of barytes which is thrown down is washed, and dried at a red heat; 100 grains of it contain, according to Berzelius, 31.8 of phosphoric acid. There is some reason to doubt whether this compound is always uniform; but there is no insoluble phosphate that is more certain, by the formation of which the analysis might be affected. The individual phosphates fall to be considered under their respective bases.

Sect. III.—*Of Phosphorous Acid.*

THIS name was given to the acid formed in the slow combustion of phosphorus in atmospheric air, and which appears in the state of a white vapour, which, attracting water from the atmosphere, is condensed, and becomes liquid. Pelletier gave the following, as the easiest method of preparing it. A cylindrical piece of phosphorus being put into a glass tube somewhat wide, a number of such tubes are placed in the mouth of a large funnel, the neck of which is inserted in a wide-mouthed bottle placed on a flat plate containing a little water. Over this is placed a large bell jar to prevent the loss of the vapour, but having two apertures at the sides to admit of the circulation of air. The phosphorus slowly absorbs the oxygen of the air; by the pieces being placed in separate tubes, the risk of the whole taking fire from the heat produced by the combustion is prevented; and the air within the jar being

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* Nicholson's Journal, vol. xxv, p. 279.

kept humid by the water beneath, the acid vapours are con-
densed, and drop through the neck of the funnel into the
bottle beneath *.

The acid prepared according to this method has a smell
slightly fœtid; its taste is extremely sour.   It instantly red-
dens, even when diluted, the vegetable colours.   When
exposed to heat, part of the water is volatilized; but as
this proceeds, a vapour is formed, which, disengaged at
the surface, affords a dense white smoke, attended with a
luminous appearance, visible in the dark.   By continuing
the heat until this ceases, the phosphorous acid is deprived
of its peculiar smell, and is converted into phosphoric.
From this experiment, some chemists have been disposed
to consider phosphorous acid as being rather phosphoric
acid, holding a portion of phosphorus dissolved, than an
immediate compound of phosphorus and oxygen in de-
terminate proportions; the luminous vapour disengaged
from it by heat being probably this phosphorus held in
solution by the watery vapour, by the loose air of the li-
quid, or by hydrogen from the decomposition of a small
portion of the water.

When this acid is combined with salifiable bases, it is
farther found that part of the compound at least is in the
state of phosphate, proving therefore the presence of phos-
phoric acid.   And, according to Dulong, the salts which
have hitherto been described as phosphites are not entitled
to this denomination, but are either phosphates, or a mix-
ture of phosphates and phosphites.

A definite compound, however, of phosphorus and
oxygen, at a lower degree of oxygenation than phosphoric
acid, and to which, therefore, the name of Phosphorous
acid may properly be given, exists.   The process to obtain
it was originally given by Sir H. Davy.   When phospho-
rus is sublimed through corrosive muriate of mercury in a

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* Mémoires de Chimie de Pelletier, tom. ii, p. 134.

glass tube, a product is obtained, which, according to one doctrine, is a definite compound of chlorine with phosphorus; according to the opposite doctrine, is composed of real muriatic and phosphorous acids, free from water. When water is added to it, muriatic and phosphorous acids are formed, the water, according to the one doctrine, imparting oxygen to the phosphorus, and hydrogen to the chlorine, so as to form these acids; according to the other, merely combining with the dry acids; while, according to the view of acidity which I have explained, the elements of the portion of water essential to their production enter into the combination in each. On exposing the liquid to heat until it become of the consistence of syrup, the muriatic acid is expelled, and the phosphorous acid remains in solution. The liquor is strongly acid, reddening deeply the vegetable blue colours, and combining with alkaline bases. It forms a white crystalline solid on cooling. When exposed to the air it absorbs oxygen, and passes slowly to phosphoric acid. When heated gently it takes fire, and burns with great brilliancy, emitting a gas which inflames on coming into contact with the air, and phosphoric acid is formed, with a red coloured matter considered as oxide of phosphorus *.

Sir H. Davy concluded, that 100 of phosphorus are combined with 75.25 of oxygen in the composition of phosphorous acid. Dulong has given almost precisely the same estimate, that of 100 with 74.88.

This acid combines with the different alkaline bases, but its salts have not been hitherto examined; those usually considered as phosphites, formed from the acid produced in the slow combustion of phosphorus, having always an intermixture of phosphoric acid. Dulong has stated a few facts with regard to them, to be afterwards

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* Philosophical Transactions, 1812. Elements of Chemical Philosophy, p. 288.

noticed under their individual history. The alkaline phos-
phites are soluble and crystallizable; those of the earths
are less soluble; they can be crystallized, however, by
spontaneous evaporation ; by concentration of their solu-
tion by heat they suffer decomposition, and are resolved
into subphosphites and superphosphites. By a stronger
heat all these salts are decomposed, phosphorus is sub-
limed with a little phosphuretted hydrogen, and a neutral
phosphate remains *.

THE acid which is formed in the slow combustion of
phosphorus is resolved, when acted on by a base, into phos-
phoric and phosphorous acids, which combine with por-
tions of the base. It might therefore be considered as
composed of these two acids in a state of intermixture.
Dulong, however, finds that it is always of uniform com-
position, that is, contains the same proportions of oxy-
gen and phosphorus ; and from this fact he concludes,
that the two acids are chemically combined, and that it is
a compound of them in definite proportions. It is to this
compound that he gives the name of PHOSPHATIC ACID.
The fact, however, from which this conclusion rests, is
doubtful. If it were established, the opinion would be more
probable, that the acid is a definite compound of phospho-
rus and oxygen, and that when it forms a phosphate and
phosphite by its action on an alkaline base, it is decompo-
sed and resolved into phosphoric and phosphorous acids.
It contains, according to Dulong's analysis, as has been
already stated, 100 of phosphorus with 109 of oxygen.
That the oxygen should be in a simple ratio to the quan-
tities in the other combinations intermediate between

* Annales de Chimie et Physique, tom. ii, p. 145.

phosphorous and phosphoric acids, the proportion would require to be 112.4; and if it be a definite compound, it is probable this is the proportion.

Sect. IV.—*Of Hypophosphorous Acid.*

THE existence of this acid, as a definite compound of phosphorus and oxygen, appears to be established. It was discovered, as has been already stated, by Dulong. Phosphorus combines, by the aid of heat, with the alkalis and alkaline earths. When these compounds are acted on by water, a portion of the water is decomposed, its hydrogen combines with a part of the phosphorus, forming phosphuretted hydrogen, which is disengaged in the gaseous form; part of its oxygen also combines with the phosphorus, forming phosphoric acid; but portions of them also combine, so as to form hypophosphorous acid. The phosphuret of barytes affords the most convenient mode of procuring it. The phosphate of barytes, which is formed when it is dropt into water, being insoluble, is precipitated; the hypophosphite of barytes is a soluble salt, and therefore remains in solution. The liquor being filtered, sulphuric acid is dropt into it, which precipitates the barytes of the hypophosphite; the acid liquor which remains may be concentrated by evaporation; a viscous fluid remains strongly acid, and incapable of crystallizing. Exposed to a stronger heat it is decomposed, phosphuretted hydrogen gas is discharged, a little phosphorus is sublimed, and phosphoric acid remains.

The analysis of this acid could not be effected by direct methods, as none of its combinations can be obtained in a dry state. The mode employed by Dulong to determine

its composition was to convert it into phosphoric acid by the agency of chlorine. The quantity necessary to produce this effect gave the equivalent quantity of oxygen; and the weight of the phosphoric acid formed being found, and the proportions of the elements of this acid being known, that of the hypophosphorous acid could be determined. Dulong inferred, that it is composed of 72.75 of phosphorus, and 27.25 of oxygen, or 100 with 37.44 [*].

This acid combines with the different alkaline bases, and its salts are distinguished by their great solubility; none of them are insoluble; those of barytes and strontites crystallize even with difficulty; that of potash is extremely deliquescent, and it, as well as hypophosphite of soda and ammonia, are soluble in alkohol in all proportions. They absorb slowly oxygen from the atmosphere, and become acid. They are decomposed by heat, giving the same products as the hypophosphorous acid itself.

Hypophosphorous acid is a powerful de-oxidating substance; even its salts precipitate the solutions of some of the metals, such as those of gold and silver, in the metallic state.

SECT. V.—*Of Phosphuretted Hydrogen.*

THIS compound, which exists as a permanent gas, was discovered by Gengembre. He obtained it in boiling an alkaline solution with phosphorus; an elastic fluid was disengaged, which had the singular property of taking fire when it came into contact with the atmospheric air [†]. Mr

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[*] Annales de Chimie et Physique, tom. ii, p. 143.
Philosophical Magazine, vol. xlviii.
[†] Journal de Physique, 1785, p. 276.

Kirwan had also, without any knowledge of the experiments of Gengembre, obtained the same gas by boiling an alkaline solution on phosphorus *. Another compound of phosphorus and hydrogen has since been discovered, to which Sir H Davy, who examined its properties, gave the name of Hydrophosphoric Gas †. As it contains a smaller proportion of phosphorus than the first, it may be named Subphosphuretted Hydrogen.

I. Phosphuretted Hydrogen.—The process followed for the production of this compound is that by which it was discovered. On phosphorus, cut into small pieces, a strong solution of potash is poured, in a retort the extremity of which terminates under water; heat is applied by a taper, and the elastic fluid is disengaged. There is some difficulty in conducting the process, as the gas is apt to explode when it mingles with the atmospheric air in the upper part of the retort; and if, to obviate this, it is filled nearly with fluid, this, on the application of the heat, comes over, and the gas is not properly produced. The best mode is to fill the vessel with hydrogen gas, previous to the introduction of the phosphorus and alkaline solution, and, to prevent any risk, to use a brass bottle instead of a glass retort.

The theory of this process is similar to that stated under the history of sulphuretted hydrogen. The alkali, by combining with the phosphorus, and by the disposing affinity it exerts, enables it to decompose a portion of the water; one portion of it attracts oxygen, forming phosphoric acid; the hydrogen evolved combines with another portion of the phosphorus, and the compound assumes the elastic form. Quicklime diffused in water, and boiled with phosphorus, likewise produces the gas : and it facilitates the operation

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* Philosophical Transactions, vol. lxxvi, p. 150.
† Ibid. 1812, p. 406.

with potash, if a little slaked lime is diffused in the liquor.
Soda has the same effect as potash, but ammonia, from its
volatility, exerts little action on the phosphorus, and ac-
quires only a slight smell *.

Dr Pearson discovered another method of producing
phosphuretted hydrogen. In his experiments on the de-
composition of carbonic acid by phosphorus, he had ex-
posed to heat phosphorus with lime : he thus formed a
compound of a reddish-brown colour ; on tasting it, he was
surprised to find it explode on his tongue, and on throw-
ing it into water, bubbles of an elastic fluid were disengag-
ed, which exploded on coming into contact with the air †.
The process for preparing this phosphuret of lime is to coat
a glass tube 8 or 9 inches long, and ½ inch wide, with clay
and sand ; to put into the bottom of it about a drachm of
phosphorus in small pieces and dry ; over this are put
small pieces of well-prepared quicklime, so as to fill the
tube, putting at the top a little pounded lime, to exclude
the air more effectually, and closing it lightly with a
plug of clay. It is then placed across a choffer or small
portable furnace, so that the middle of the tube is rais-
ed to a red heat ; the phosphorus at the end of the tube is
thus sufficiently heated to be volatilized, and passing over
the red hot lime, it enters into combination with it, a small
portion generally escaping from the mouth of the tube, and
taking fire. The phosphuret of lime is of an auburn co-
lour ; it is kept in bottles well stopt, to exclude the access
of humidity. When thrown into water, bubbles of phos-
phuretted hydrogen gas are rapidly produced, which flash
as they rise from the surface of the fluid, the lime in this
preparation enabling the phosphorus to decompose the wa-
ter, as the alkali does in the other. Dr Pearson found, that
by a process similar to the preceding, a dry phosphuret of
potash can be prepared, which thrown into hot water pro-

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* Journal de Physique, tom. xxvii, p. 280.
† Philosophical Transactions, 1792, p. 303.

duces a similar inflammable gas; and a similar combination of phosphorus with barytes and strontites, exerting the same agency, may be formed.

The gas obtained by these different methods is not equal in purity. That produced by the action of the solution of potash on phosphorus, seems to contain a considerable portion of subphosphuretted hydrogen, and as first produced does not even inflame spontaneously in the air; the addition of the lime causes it to be evolved more pure; from the action of dry phosphuret of lime on water it appears to be produced nearly in a state of perfect purity : And according to Dr Thomson's experiments, this affords the best process, adding at the same time to the water a little muriatic acid. A tubulated retort may be filled to the tubulature with water, recently boiled and containing a fourth of muriatic acid; phosphuret of lime is to be quickly dropt in, the stopper introduced, and the neck of the retort filled with water. The gas is then disengaged, and may be collected, and the action may be aided by a very gentle heat *.

Phosphuretted hydrogen is permanently elastic; its specific gravity, according to Dalton, is .85, atmospheric air being 100. Davy makes it not higher than .34 ; but this must have been owing to an impure gas having been employed. Dr Thomson found it in different experiments to be .865, and in one which he regarded more accurate 903.

Phosphuretted hydrogen gas has an unpleasant smell; its taste is intensely bitter. It is absorbed by water in small quantity; 100 cubic inches absorb, according to Dr Henry, 2.14 cubic inches of gas ; according to Mr Dalton about 3.7. The smell of the solution is disagreeable; its taste very bitter; its colour is a pale yellow   The gas is expelled from it by heat, unchanged; it has no effect on the vegetable colours ; by exposure to the air it is decompos-

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* Annals of Philosophy, vol. viii, p. 89.

ed. It decomposes a number of the metallic solutions, and throws down dark coloured precipitates, which appear in general to be metallic phosphurets.

The most characteristic property of phosphuretted hydrogen gas is its high inflammability; this it derives from the phosphorus it contains being in the most favourable state for combining with oxygen,--deprived of cohesion, and not retained by any strong affinity. The moment it comes in contact with atmospheric air it inflames with a vivid flash of light and a slight explosion; nor can they be presented to each other with safety, but in small quantities. If bubbles of the phosphuretted hydrogen gas be received successively in oxygen gas, the combustion is still more vivid, and the explosion, at the breaking of each bubble, is such as to convey a sensible impression to the hand placed on the jar. This gas likewise inflames when received in oxymuriatic acid gas; nitric oxide gas produces, when mixed with it, a white vapour, and diminishes its inflammability *; but if oxygen be added immediately, the heat from its combination with the nitric oxide is sufficient to cause inflammation. An accident, producing severe injury, happened to Pelletier from making a mixture of this kind of these three gases †. The mixture of phosphuretted hydrogen with nitric oxide gas alone, and also that with nitrous oxide, is inflamed with detonation by the electric spark.

A singular and beautiful appearance presents itself in the inflammation of this gas in atmospheric air. When the bubble of gas breaks, there is a flash of light, and this is accompanied with a dense white vapour, which rises in the atmosphere, extending itself circularly, so as to form a horizontal ring; this ascends in a calm atmosphere to the height of several feet, enlarging as it rises, so that before it

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* Philosophical Transactions, vol. lxxvi, p. 152.
† Mémoires de Chimie, tom. i, p. 313.

breaks it is often more than a foot in diameter. This white cloud consists of watery vapour wafting phosphorous acid, the one being produced by the union of the oxygen of the atmosphere with the hydrogen of the gas, the other by its union with the phosphorus; but it is somewhat difficult to account for this regular appearance being assumed. Probably, as Dr Higgins has expressed it, " the flocculent " phosphoric acid, and aqueous vapour, may be thrown by " the eccentric impulse of the explosion into the form above " described, and buoyed in the air until the ring is cooled " or dissipated *."

In receiving this gas in a jar over mercury, and afterwards transmitting into it successive small portions either of atmospheric air or oxygen gas, the vivid inflammation is at first produced; but Gengembre observed, that the gas at length no longer inflames, though it is still capable of burning brilliantly when kindled in contact with atmospheric air; a proof that the phosphorus of the phosphuretted hydrogen is more disposed to burn at a low temperature than the entire compound, and that, in the combustion, a portion of the hydrogen, retaining a portion of phosphorus, does not burn †. Mr Dalton submitted to more minute examination, the results of the action of the two gases. He found, that the phosphuretted hydrogen may be entirely consumed by burning it either with one volume or with one volume and a half of oxygen gas. In the first proportion, the products are water and phosphorous acid: in the second they are water and phosphoric acid. If less oxygen be employed, part of the gas remains unconsumed ‡.

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* Minutes of a Society for Philosophical Exper. p. 278.

† Journal de Physique, tom. xxvii, p. 278.

‡ Chemical Philosophy, p. 461. Mr Dalton has since stated, that two volumes of oxygen are necessary to the complete combustion of phosphuretted hyd ogen, the products being water and phosphoric acid, (Annals of Philosophy, vol. xi, p. 8.).

Dr Thomson finds, that if half a volume of oxygen gas be added to a volume of phosphuretted hydrogen gas, the whole of the phosphorus is consumed, and there remains a volume of hydrogen gas. The action of the compound gases which afford oxygen, such as nitric or nitrous oxide, corresponds to these results. For complete combustion three volumes of either of these gases are necessary; the products are phosphoric acid and water, with three volumes of nitrogen from nitrous oxide, and one volume and a half from nitric oxide.

Phosphuretted hydrogen is decomposed by potassium. When the latter is heated in it, a phosphuret of potassium is formed, and hydrogen is evolved. According to Gay-Lussac, there is an enlargement of volume when an excess of the gas is present; but none when there is an excess of potassium, owing to hydrogen being absorbed by the potassium [*]. But this is doubtful. If sulphur be heated in the gas it combines with the phosphorus, and another portion combines with part of the hydrogen, forming sulphuretted hydrogen.

Phosphuretted hydrogen is decomposed by the agency of the electric spark; the phosphorus is precipitated of a reddish or brown colour. The hydrogen gas remains without any change of volume. When any enlargement has been observed, it has probably arisen from the presence of moisture.

From this analysis, as well as from that by oxygen, it is evident that this gas is a compound of phosphorus and hydrogen, containing its own volume of hydrogen. The proportions of its elements, therefore, are discovered from the difference between its specific gravity and that of pure hydrogen, this difference giving the weight of the phosphorus in a given volume. From this mode of estimation

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[*] Recherches Physico-Chimiques, t. i, p. 210. 215.

Dr Thomson infers that it is composed of 1 of hydrogen and 12 of phosphorus *.

II. Subphosphuretted Hydrogen.   It was known that the gas disengaged on first applying heat to a solution of potash on phosphorus, is less inflammable than the proper phosphuretted hydrogen ; it merely produces a white vapour on escaping into the atmosphere, without any sensible illumination.   It was also found, that the phosphuretted hydrogen differed considerably in specific gravity, and in the quantity of oxygen consumed in its combustion, according to the circumstances of its formation.   These facts appeared to prove, that phosphorus and hydrogen combine in different proportions.   Mr Dalton supposed that these diversities are owing to the intermixture of hydrogen.   But it is not probable that pure hydrogen should be evolved in the processes by which this gas is formed ; and the proof he has given of the intermixture of hydrogen, that of their being a residue of it when the gas is agitated with liquid oxymuriate of lime, is defective, since the action of the oxymuriate may subvert the composition of the proper compound, and cause hydrogen to be evolved.

A gas of uniform properties and specific composition appears to be produced, by a process given by Sir H. Davy, already pointed out (page 393,) that of submitting the hydrophosphorous acid to a moderate heat : a portion of the water may be supposed to be decomposed by the excess of phosphorus ; its oxygen converts one portion of the phosphorous acid into phosphoric acid, and its hydrogen abstracts another portion of the phosphorus, and forms a

* Annals of Philosophy, vol. viii, p. 90.

compound which is disengaged in the elastic form *. To this compound Sir H. Davy gave the name of Hydrophosphoric Gas; that of Subphosphuretted Hydrogen is more conformable to analogy, and denotes better its relation to phosphuretted hydrogen.

This gas has a smell which is disagreeable, but not so strong as that of phosphuretted hydrogen: its specific gravity appears to be about 0.87, atmospheric air being 100. Water absorbs about one-eighth of its volume of it. It does not inflame spontaneously in atmospheric air or oxygen gas, but if heated in mixture with atmospheric air to 212° it explodes, and heated with oxygen gas it detonates with great violence. Three measures of it consume rather more than five measures of oxygen gas, and even when the oxygen is in excess a little phosphorus is precipitated. It inflames spontaneously in oxymuriatic gas. Potassium heated in it combines with its phosphorus, pure hydrogen gas remains, and the volume is doubled. When sulphur is sublimed in the gas the volume is also doubled, a compound of sulphur and phosphorus is formed, and the elastic fluid is sulphuretted hydrogen. It is obvious, from these results, that this compound consists of phosphorus combined with two volumes of hydrogen gas which are condensed into one volume. The proportions by weight are stated by Davy at 4.5 of hydrogen, with 22.5 of phosphorus. It is from this condensation that its specific gravity is equal to that of the other compound, and that it combines with so large a quantity of oxygen.

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* Philosophical Transactions, 1812.

SECT. VI.—*Of Phosphuretted Sulphur.*

SULPHUR and phosphorus combine apparently in inde-
terminate proportions, forming what may be named a Phos-
phuret of sulphur, or a Sulphuret of phosphorus, according
to the excess of either ingredient. The combination was
first observed by Margraaf, and was afterwards examined
by Pelletier *. ·

It may be effected by the application of heat to the
phosphorus and sulphur, but this is attended with some
risk. If the two substances be put into a retort connect-
ed with a receiver, on applying heat, the combination, Pel-
letier remarked, takes place with such violence, that a por-
tion of the mixture is thrown from the retort with an ex-
plosion, and the vessel is frequently broken. The method
he employed was to put them into a matrass with water,
and apply heat sufficient to melt the phosphorus; its com-
bination with the sulphur then takes place with less vio-
lence; though even in this way, he remarked, that some-
times part of the compound was thrown from the matrass,
particularly when about equal parts of sulphur and phos-
phorus were used, and when the heat was too quickly ap-
plied.

This compound is more fusible than phosphorus. The
fusibility is greatest when they are in equal proportions,
the compound melting, or rather, when liquid, congealing
at a temperature of $41°$; with one of sulphur to two of
phosphorus, it congeals at $50°$; and with 1 to 4 at $60°$;
when the sulphur exceeds an equal weight, it becomes less
fusible; the compound of one of phosphorus with two of
sulphur congeals partially at $56°$, and that of one of phos-
phorus with three of sulphur at $99°$.

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* Mémoires de Chimie, tom. i, p. 281.

Pelletier observed that it has a tendency to decompose water. The water kept over it became in a few days strongly acid; and the decomposition was indicated by a fœtid odour, in which that of sulphuretted hydrogen and of phosphuretted hydrogen could be distinguished, and by the disengagement of a vapour which appeared luminous in the dark [*].

This decomposition of water, and production of a gas easily inflamed, appeared to be established from an accident related by Mr Accum, from an experiment in which half an ounce of phosphorus cut in small pieces had been introduced into a Florence flask, containing about ten ounces of water and one ounce of sulphur. Heat having been applied, and continued a little after the union of the sulphur and phosphorus had been effected, the flask became filled with dense white fumes, and, on agitating the fluid, the whole exploded with much violence. By applying the heat gradually to a mixture of phosphorus and sulphur with water, in a Wedgwood's tube, terminating by a bent tube in the mercurial trough, a large quantity of gas was collected, which inflamed when mixed with atmospheric air, producing sulphur, sulphuric acid and phosphoric acid [†].

Dr Briggs confirmed these facts by some additional observations. The decomposition of the water commences when the union of the sulphur and phosphorus takes place; and if the temperature is raised to 210, is very rapid, the gas disengaged being highly luminous in the dark, and holding sometimes dissolved so much phosphorus as to take fire on coming into contact with the air, and form the ring of white vapour, which the combustion of pure phosphuretted hydrogen displays [†]. He supposed, that the compound formed under water is not a pure phos-

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[*] Mémoires de Chimie, tom. i, p. 294.
[†] Nicholson's Journal, vol. vi, p. 1.   [‡] Ibid. vol. vii, p. 58.

phuret of sulphur, or sulphuret of phosphorus ; but that
these bases are in the state of oxides, having received oxy-
gen from the water, whence their greater inflammability.
He also gave a process by which the sulphur and phos-
phorus may be combined with safety in the dry way, form-
ing a product somewhat different.   It consists in filling a
glass tube with sulphur and phosphorus, corking it firm-
ly, and plunging the tube into warm water, the heat of
which is to be gradually raised until it boil.   The sul-
phur and phosphorus unite without violence ; and, after
removing the tube from the water, it is to be shaken that
the mixture may be complete.   It is necessary, however,
to be cautious, in attempting to perform an experiment of
this kind.

This compound, when a small proportion of sulphur
has been used, is solid when cold, has a crystallized ap-
pearance, and a yellowish white colour, while that formed
under water has a friable texture, spongy appearance, and
a sulphur-yellow colour.   The former, though more in-
flammable than phosphorus, is not so much so as the lat-
ter ; but it may be rendered equally inflammable, by set-
ting fire to it while it is still in the tube in which it has
been prepared, by plunging a hot wire into it, and allow-
ing it to burn for 5 or 6 seconds.   It is thus, as Dr Briggs
supposed, converted into an oxide of sulphur and phos-
phorus, and is so inflammable, that the instant a little of it
is brought into the air, it catches fire.   From the great
inflammability of these compounds, they are used for pro-
curing a lighted match, and form the best kind of phos-
phoric match bottles.   The proportion used for this pur-
pose is said by Mr Accum to be one part of sulphur with
eight of phosphorus ; but less of sulphur, as a thirtieth, is
preferable, as the compound is equally inflammable, and
is less soft.   Phosphorus alone kindled in a close bottle,
by a hot iron wire, and stirred so as to adhere to the sides,
forms a crust so inflammable, that it kindles when a little

is withdrawn on a match, but it soon loses this power from becoming humid. The intermixture of a little quicklime is useful by preventing this.

It is not easy to determine in what proportions sulphur and phosphorus combine, as from their fusibility, and that of their compounds, they appear to unite in any relative quantity in which the one is presented to the other. Mr Faraday has found, that when these compounds are kept in contact with liquid ammonia, the impurities are removed, and the matter becomes of a lighter colour, semitransparent, and more fluid. A compound of this kind, composed of five of sulphur, and seven of phosphorus, remained liquid at 32 ; and after having stood some weeks, deposited crystals of sulphur, a portion of it remaining less fusible, and which at length became a crystalline mass. This having parted with its excess of sulphur, might perhaps be regarded as a definite compound *.

CHAP. V.

OF BORACIC ACID.

This acid is one of comparatively limited distribution. It has been found in small quantity as a volcanic product, and in the water of some lakes in volcanic districts ; and it occurs as a constituent part of a few minerals. But the source from which it has always been obtained is a native compound of it with soda, the Borax of commerce, a salt found in Thibet, and which has long been imported into

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* Journal of the Royal Institution, iv, p. 361.

Europe for the uses to which it is applied. Homberg and Lemery first obtained the acid from it, and Geoffroy shewed that soda is its base.

To procure the boracic acid from this salt, two processes are followed. If the borax be dissolved in hot water, and half its weight of sulphuric acid be dropt into the solution, on cooling, small soft scales are deposited, and by evaporation a larger quantity is procured. These are the boracic acid, the sulphuric acid having combined with the soda of the borax; they are washed with cold water to carry off any adhering sulphuric acid or sulphate of soda, and are dried. Another process is to add one part of sulphuric acid with an equal weight of water, to two parts of borax in powder, in a retort. On applying a moderate heat, the boracic acid is sublimed with the watery vapour, and the greater part of it condenses in scales in the neck of the retort. By this latter process a small quantity of the acid only is procured; and by the former it is not obtained in a state of purity, portions both of the base with which it was united, and of the acid by which it is precipitated, adhering to it. It may probably be obtained purer by employing nitric acid in its precipitation, and afterwards exposing it to a red heat. Gay-Lussac and Thenard employed muriatic acid, and by melting the boracic acid in a platina crucible obtained it pure.

The composition of Boracic Acid remained unknown until within these few years. Gay-Lussac and Thenard submitted it to the action of potassium aided by heat, and found an olive-coloured substance to be produced, which they considered as arising from the acid having been decomposed by the abstraction of its oxygen by the potassium; and in prosecuting these researches they discovered the substance which appears to be its base, and examined its principal properties. Their process consists in exposing to heat in a copper tube, to which a bent glass tube is adapted, equal weights of pure and dry boracic acid and

potassium; the heat is raised to redness, and is kept at this for a few minutes; the operation is then complete. When the temperature has risen above 300°, the mixture becomes suddenly ignited. During the experiment, there is only expelled with the air in the tube a few bubbles of hydrogen gas, not equal to the thirtieth part of what the potassium would produce by its action on water. All the potassium and a portion of the acid disappear, and are converted into a substance of an olive gray colour, having an earthy appearance, strongly alkaline, which, submitted to the action of water, produces scarcely any sensible effervescence, but is in a great measure dissolved; the dissolved matter is potash and borate of potash; the undissolved matter is of a grayish green colour, flocculent, and is the substance which they regarded as the radical of the boracic acid.

Sir H. Davy, in submitting boracic acid to galvanic action, had observed a dark coloured inflammable substance to be separated in minute quantity at the negative wire. He afterwards found, that on heating boracic acid with potassium, a similar substance was produced, and borate of potash was formed. Both appearances he observed indicated decomposition of the acid, but the quantities were too small to admit of the products being examined; and the appearance from the action of the potassium he supposed might even be accounted for from the impurity of the acid, without supposing its actual decomposition. He afterwards performed the experiment of heating potassium with boracic acid on a larger scale, and obtained results the same as those which had been obtained by Gay-Lussac and Thenard *.

To the substance obtained by these methods the French chemists gave the name of Bore. Boracium was proposed by Davy; that of Boron has been preferred, as more con-

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* Philosophical Transactions, 1809.

formable to analogy.   The following are its properties, as
ascertained by Gay-Lussac and Thenard *.

It is best procured by boiling the product of the mutual
action of the acid and the potassium in water for some
minutes, to dissolve the potash and borate of potash ; and
saturating the excess of alkali by muriatic acid, to pre-
vent its re-action on the boracic radical.   The boron
slowly subsides; it is washed with water, and dried with a
moderate heat.   It is of a greenish-brown colour, insipid,
and does not affect the vegetable colours.   It neither melts
nor volatilizes at a high degree of heat; it is insoluble in
water, in alkohol, or in oils cold or warm.   It does not
decompose water at a temperature near to that of boiling.
It exerts no action on oxygen at an ordinary temperature,
but when heated suffers combustion.   In oxygen gas its
combustion is vivid, and the oxygen is rapidly consumed.
The combustion takes place in atmospheric air at a red
heat, but less vividly, and in both there is some obstacle
to the entire combustion, from the acid which is formed
vitrifying at the surface.   There is a very considerable
augmentation of weight, without any evolution of gas, and
boracic acid is formed, which by solution in boiling water
and evaporation may be crystallized.   It is not acted on
by dry oxymuriatic acid gas.   Nitric acid is decomposed
by it with rapidity, there is an evolution of nitrous gas,
and the boron passes to the state of boracic acid.   It decom-
poses sulphuric acid when aided by heat; and at a high
temperature it takes oxygen from a number of compound
salts, nitrates, sulphates and carbonates.   It also reduces
a number of metallic oxides.   It appears to combine with
a large proportion of oxygen to form boracic acid.   From
its oxygenation by nitric acid, Gay-Lussac and Thenard
infer that the acid contains one-third of its weight of oxy-

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* Mémoires d'Arcueil, tom. ii, p. 312.   Recherches Physico-
Chimiques, tom. i, p. 298.

gen, of course 100 of boron are combined with 50 of oxygen.

The account given by Sir H. Davy of the properties of this substance is nearly the same, with the addition of a few facts. Though it is not fused by a heat raised to whiteness, it sinks after this operation rapidly in sulphuric acid, which it does not do before. It burns brilliantly, he states, in oxymuriatic gas at common temperatures; but this appears to be a mistake, and the opposite one by the French chemists is correct. It appears to combine with sulphur by fusion, and with the fixed alkalis both by fusion and solution. He found that in the production of this substance twenty grains of potassium had their inflammability destroyed by eight grains of the acid, a proof that it exists in the acid combined with a large quantity of oxygen. He inferred from some analytic and synthetic experiments, that the proportions are nearly 1 of boron to 1.8 of oxygen.

The very different proportions of the elements in the composition of this acid assigned by Gay-Lussac and Davy, shew sufficiently the difficulty of determining them with accuracy. Davy supposes, that the quantity of oxygen is under-rated in the method employed by Gay-Lussac and Thenard, from a portion of the acid being volatilized along with the nitric acid. On the other hand, the difficulty of producing the complete oxygenation of boron by combustion, renders that mode of experiment liable to error. Berzelius endeavoured to determine the composition by a different method,—that of finding the quantity of base which the acid neutralizes, and from this inferring the quantity of oxygen, on the principle already explained. He concluded, that 100 of boracic acid contain 73 of oxygen, which agrees nearly with Davy's estimate [*]. On the other hand, Gmelin, from an analysis of some of the borates, has more lately inferred that the acid is composed of 74.4 of boron

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[*] Annals of Philosophy, vol. iii, p. 57.

with 25.6 of oxygen *. All these results must, therefore, be considered as uncertain. The calculation too, from the constitution of the borates, applies to what is called the real acid; while it appears, from the experiments of Berzelius, that it contains a quantity of water essential to its constitution; in other words, is a ternary compound of boron, oxygen and hydrogen.

Gay-Lussac and Thenard found that boracic acid is not decomposed by charcoal at a high heat. But Descostils had observed, that in exposing to the heat of a forge, mixtures of the acid with charcoal, and iron, or platina, metallic masses were obtained, which when treated by nitromuriatic acid gave sensible quantities of boracic acid. And it is not improbable, that some of the changes observed to be produced in metals, in operations in which borax had been employed as a flux, may have been owing to a decomposition of the acid, and an alloy of boron. Dobereiner has given a method by which boron, he affirms, may be obtained from the acid by the agency of charcoal. It consists in reducing fused borax to a fine powder, mixing it with a tenth of its weight of lamp black, and exposing the mixture in a gun-barrel with a bent tube to a white heat for two hours. Carbonic oxide is formed in abundance, and at the end of the operation a compact mass is found of a grayish-black colour, which when submitted to repeated washings with boiling water, and one affusion of muriatic acid, gives a powder of a greenish-black colour, exhibiting the same properties as boron, but only mixed with a little charcoal. Dobereiner supposes, that the operation is principally effected by the charcoal reducing the soda of the borax, and the sodium decomposing the boracic acid; an addition of soda, therefore, with a larger proportion of charcoal, may promote it. If the process succeeds it will

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* Annals of Philosophy, vol. ix, p. 25.

afford an economical mode of procuring boron, though not in a state of perfect purity *.

Boron had not been combined with hydrogen. Gmelin has rendered it probable that such a combination may be established. On fusing iron-filings with one-tenth of boracic acid in a crucible, a metallic mass was obtained of a silvery white colour, which dissolved, though with difficulty, in muriatic acid. The gas disengaged had a smell different from that of pure hydrogen, and burned with a green flame. From this latter fact, in particular, the presence of boron might be inferred †.

Boracic Acid, obtained by the process above described, is in brilliant white scales, soft to the touch; its taste is bitterish, with a slight degree of sourness; it reddens the vegetable colours. It is not altered by exposure to the air. It is stated to be soluble in 20 parts of cold water, and in 5 of boiling water: according to Davy, more than 50 of boiling water are required for its solution. It is soluble in alkohol, and, what is a very distinctive character of it, gives to the flame of alkohol in burning a green colour.

Exposed to a moderate heat it swells; when the heat is raised to redness, it is fused into a glass, which remains transparent while liquid; when cold, it retains its acid properties, and is soluble again in water. By the most intense heat it is not volatilized; but if a small quantity of water be present, the aqueous vapour carries with it a considerable portion of the acid. Hence the practicability of obtaining it by sublimation, according to one of the processes above described. It retains like other acids a portion of combined water; Davy having found, that after exposure to the heat of a forge, globules of hydrogen are obtained, when it is heated with dry iron-filings. And in its usual

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* Annales de Chimie et Physique, t. ii. p. 214.
† Annals of Philosophy, vol. ix, p. 25.

crystallized form, the acid appears to be combined with a considerable quantity of water. The compound of boracic acid and water, Sir H. Davy states, appears from his experiments to contain about 57 of acid to 43 of water. According to Berzelius, boracic acid contains two proportions of water, one of crystallization, the other of composition. By a moderate heat the former is expelled; by a stronger heat half of the latter he states is driven off, and by a red heat the hydrate is entirely decomposed. It loses 22 per cent. at a heat exceeding somewhat that of boiling water, and in combining with a base such as oxide of lead it loses 44 *.

Boracic acid combines with the alkalis and several of the earths, forming compounds named Borates. These salts retain in general the property of communicating a green colour to the flame of alkohol. They are decomposed by all the acids, the carbonic excepted, in the humid way. In the dry way, the boracic acid, from its great fixity, is able at a high temperature to decompose several of those salts, the acid of which has a tendency to assume the gaseous form. Its attractions appear stronger to the earths than to the alkalis. The alkaline borates are very soluble in water, while the earthy are the reverse.

Boracic acid scarcely acts on the metals; but it may be combined with their oxides by complex affinity. The mode of effecting this is to mix a solution of the metal in nitric acid, with a solution of borax; the boracic acid unites with the metallic oxide, the nitric acid combining with the soda. These combinations, so far as they have been examined, are afterwards to be described.

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* Annals of Philosophy, vol. iii, p. 57.

CHAP. VI.

OF MURIATIC ACID, AND ITS COMBINATIONS.

THIS acid has been long known as an important chemical agent, equal nearly in energy of action to the sulphuric and nitric. It exists when uncombined in the gaseous form, and in a state of combination is extensively distributed in the mineral kingdom. The combination of it with soda forms the neutral salt, which is the principal ingredient in the water of the ocean, and which also exists in immense strata in the earth as a mineral deposite, forming rock salt. Its saline compounds are common ingredients in mineral waters. It serves to mineralize some of the metals. And it is found in a number of the products of the vegetable and animal systems.

The radical of this acid is unknown, all the usual methods of analysis having failed in effecting its decomposition. A doctrine has been maintained, however, with regard to it, in which it is considered as a compound of hydrogen with Oxymuriatic acid or Chlorine, a substance formerly supposed to be a compound of muriatic acid and oxygen, but which, according to this view, is regarded as a simple body. Hyperoxymuriatic or Chloric Acid, and Euchlorine, are compounds of the same radical with other proportions of oxygen. The history of these substances and of their combinations are the subjects of the following sections.

Sect. I.—*Of Muriatic Acid.*

MURIATIC acid is usually procured from sea salt decomposed by sulphuric acid ; the sulphuric acid combines with the soda the base of the salt, and the muriatic acid is disengaged even without the application of heat. It assumes the gaseous form, and is received over quicksilver, as water instantly absorbs it in large quantity. It forms a permanent gas, invisible while water is excluded, but condensing on the contact of water, and therefore forming white vapours when presented to the atmosphere, by combining with the vapour diffused in atmospheric air.

To discover the composition of this acid has always been an object of interest to chemists. It was inferred from analogy to contain oxygen ; but nothing was determined by the common modes of analysis with regard to its base. Priestley had observed the production of hydrogen from it by the action of metals, and also by electricity. Girtanner observing the same fact, that hydrogen is evolved when it is submitted to the action of substances having a strong attraction to oxygen, supposed it to be a compound of these two elements. But, from the experiments of Van Marúm, Tassaert, and Henry, this evolution of hydrogen appeared to be connected with the presence of water in the acid,· and to arise from its decomposition : and the quantity of it was comparatively inconsiderable.

The progress of investigation proved, however, that the relation of water or of hydrogen to this acid is more important than had appeared from these experiments. This was first established by the researches of Gay-Lussac and Thenard. They shewed, that a large proportion of water is deposited when the acid in its gaseous state passes into chemical combination ; that when transmit-

ted, for example, over oxide of lead, or oxide of silver, it affords a quantity equal to a fourth of its weight : And it cannot be obtained insulated without water. Its salts, they found, cannot be decomposed at a very high temperature, either by the vitreous superphosphate of lime, or by boracic acid; whence they concluded, that even sulphuric acid, if deprived of water, probably could not decompose them. It exists in its real or dry state only in combination with other bodies, and they observed the properties of a singular compound of this kind formed by the action of phosphorus on calomel and on muriatic acid gas, which they considered as composed of the dry acid, oxygen and phosphorus *. Mr Davy confirmed these results. He found that muriatic acid could not be expelled from perfectly dry muriate of lime by heating it with dry sulphate of iron, or with vitreous phosphoric acid, or boracic acid; but if water were added, it was disengaged rapidly. He endeavoured to separate the dry acid from muriate of tin, by heating the muriate with sulphur and with phosphorus, but he obtained only compounds which did not redden litmus paper, but evolved muriatic acid gas on the contact of water. And similar compounds were obtained from the muriates of mercury with the same inflammables†.

There is another class of facts of the first importance in relation to the constitution of muriatic acid, first elucidated likewise by the researches of the French chemists. Muriatic acid, when submitted to the action of substances which impart oxygen readily,—when distilled, for example, from black oxide of manganese, is converted into a product which exists in the gaseous form, and is distinguished by very peculiar properties. This substance, from the nature of the processes by which it is obtained, and

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* Mémoires d'Arcueil, tom. ii, p. 307, 320, 322. Nicholson's Journal, vol. xxiv, p. 31, 98.
† Philosophical Transactions, 1809.

also from its apparent analysis, had been regarded as a
compound of muriatic acid and oxygen, and as such it
had been denominated Oxymuriatic Acid. Gay-Lussac
and Thenard made the important experiment of submit-
ting it to the action of hydrogen,—mixing oxymuriatic gas
and hydrogen gas in equal volumes, and exposing the
mixture to the chemical agency of light. It was entirely
converted into muriatic acid gas without any change of
volume, and without any deposition of water. Supposing,
therefore, that oxymuriatic acid is a compound of muria-
tic acid and oxygen, it follows, that in this experiment
its oxygen combines with the hydrogen, and forms water,
which remains in combination with the acid, constituting
muriatic acid gas; and from the known specific gravities
of the gases, they inferred, that the quantity of water must
be equal to 0.245 of its weight. Oxymuriatic acid, they
found reason to conclude, contains no combined water;
they therefore endeavoured, by abstracting its oxygen, to
obtain muriatic acid free from water. The metals could
not be employed, as when oxidated they combine with the
acid. They employed the sulphurets, but obtained a com-
pound from which muriatic acid could be obtained only
when water was supplied. With phosphorus they obtain-
ed a similar result. Lastly, they endeavoured to decom-
pose the oxymuriatic acid gas by passing it over calcined
charcoal at a red heat : at first it was converted into mu-
riatic acid by the action of the portion of hydrogen remain-
ing in the charcoal; but this effect diminished, and the gas
at length passed without alteration, a proof that pure car-
bon does not decompose it, or abstract its oxygen.

From these facts, these chemists concluded, that muria-
tic acid cannot exist in the gaseous state without water,
and that oxymuriatic acid cannot be decomposed but by
bodies which contain hydrogen, or by those which like the
metals, sulphur or phosphorus, can form with it ternary
compounds. In conformity to this they found, that it is

not decomposed by sulphurous acid, carbonic oxide, nitrous oxide, nor nitric oxide, if they are perfectly dry; but that it is immediately decomposed by these substances by the medium of water. They found, that in its conversion into muriatic acid and oxygen, by the action of solar light, the presence of water is equally necessary. These experiments, they add, give a view of the constitution of oxymuriatic acid, altogether different from what had been before received. It had been regarded as a body the most easy of decomposition, while it appears, on the contrary, to resist the action of the most powerful agents, and to be incapable of being converted into muriatic acid, but by the medium of water or of hydrogen.

While admitting this view, conformable to the opinion which had been hitherto received of the relation between oxymuriatic and muriatic acid, they at the same time suggested another, as following from these facts,—that oxymuriatic acid may be a simple substance, implying, of course, that muriatic acid is a compound of it with hydrogen. This hypothesis they had illustrated in their memoir, but it appeared so extraordinary, that Berthollet prevailed on them to announce it with reserve. Gay-Lussac continued, however, to present it as the more probable opinion, and it was adopted by Dulong and Ampere [*].

Sir H. Davy some time afterwards adopted the idea suggested by the French chemists, and instituted a series of experiments which confirmed it. He employed various methods to abstract oxygen from oxymuriatic acid, but without any successful result, when no substance was introduced which might afford oxygen from another source. In submitting, for example, the compound formed by heating it with tin, to the action of ammonia, a combination was established, from which no oxide of tin could be obtained.

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[*] Mémoires d'Arcueil, tom. ii, p. 357. Annales de Chimie, tom. xci, p. 97.

And in submitting the products formed by the action of oxymuriatic gas on phosphorus, and on sulphur, to the action of ammonia, no abstraction of the acids formed by the oxygenation of phosphorus or sulphur could be effected. Thus, no evidence was obtained of the presence of oxygen in oxymuriatic gas. It might therefore be regarded as a simple substance, which combined with hydrogen forms muriatic acid, and hence as an acidifying element belonging to the same class as oxygen. On this view of its nature, the name oxymuriatic acid could not be properly applied to it. He gave it, therefore, from one of its most characteristic qualities, its yellowish green colour, the name of Chlorine *.

According to this doctrine, then, oxymuriatic acid is held to be a simple substance, and muriatic acid a compound of it with hydrogen. The substances formed by its action on inflammables and metals are compounds of it with the metal or inflammable body. The liquid formed, for example, when phosphorus is inflamed in oxymuriatic gas, is a compound of chlorine and phosphorus; and the solid matter obtained when potassium or tin burns in the gas, is a compound of these metals with chlorine. The

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* Sir H. Davy has said, that Scheele is the author of the doctrine that chlorine is a simple body, and that muriatic acid gas is a compound of it with hydrogen ; and that in his observations he merely followed and extended Scheele's views. —Scheele had not the most distant conception of this doctrine; nor was it possible he could, for all the facts necessary to establish it, or even to convey an idea of it, were unknown to him. He knew nothing of the peculiar relation of water to muriatic acid, or even of the existence of muriatic acid in the gaseous form : the composition of water was equally unknown to him. Even the slight sanction that might be given to this assertion by the opinion which was at one time maintained, that hydrogen is phlogiston, does not apply ; for that opinion

same products can often be obtained by the action of muriatic acid gas, the hydrogen of the acid in this case being liberated, and the chlorine combining with the metal. Or, if muriatic acid is presented to these substances in an oxidated state, to potash for example, or oxide of tin, the hydrogen of the acid combines with the oxygen of the oxide and forms water, while the metallic base enters into union with the chlorine.

According to the opposite view, oxymuriatic acid is a compound of muriatic acid and oxygen; and muriatic acid gas is a compound of muriatic acid and water, conformable to other acids, which in their insulated form hold water in intimate combination. Muriatic acid acts on the different salifiable bases, alkalis, earths, and metallic oxides, exactly as other acids do; it combines with the base, potash or oxide of tin, for example, and its combined water is liberated. When it acts on them in their metallic form it forms the same products, the metal receiving the oxygen of its combined water, so as to form the oxide which then unites with the acid, and the corresponding hydrogen is disengaged. Or, lastly, when oxymuriatic acid acts on these substances, its oxygen is communicated

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was never held by Scheele, nor was known to him, but was advanced at a subsequent period by Kirwan. Scheele speaks of phlogiston being present in muriatic acid exactly as he speaks of it being present in sulphurous acid, or in nitrous acid : the term had no allusion to hydrogen ; it was only conveying the idea which was afterwards expressed by the word de-oxygenated, and the dephlogisticated muriatic acid of Scheele is merely the synonime of the oxygenated muriatic acid of Berthollet. Gay-Lussac and Thenard suggested the new doctrine, of which, previous to their announcing it, no chemist had the most remote idea, nor could have had, but from the facts which they had at the same time discovered,—those, in particular, that oxymuriatic gas is not decomposed by charcoal, and that with hydrogen it forms muriatic acid gas alone.

to the metal, and the oxide produced combines with the acid; or, if acting on an oxide, its oxygen is liberated and the same compound is formed.

A few observations on the comparative merits of these views will be necessary to determine, on the most probable grounds, the constitution of the acid, before proceeding to its chemical history.

From the contrast of the two theories, it is evident, that the leading question is, Does muriatic acid contain combined water or not? If it do, the old doctrine must be admitted; if not, the other may be maintained. In support of the affirmative in this question, there is the obvious analogy, that all the other powerful acids contain combined water, and hence it would be singular if muriatic acid did not. But besides this, the fact is established by the very same evidence as that by which it is established, and which is held conclusive, with regard to the others. When sulphuric or nitric acid in the highest state of concentration is combined with a base, a portion of water is liberated. When muriatic acid gas is combined with the same base, there is the same result, nor is the quantity of water inferior to that afforded by the others. This fact is admitted as conclusive in proving the presence of water in the former: it ought equally therefore to be admitted as conclusive in proving its presence in the latter. It is true that the production of water in the case of muriatic acid may be accounted for on another assumption, that of supposing the acid to be decomposed, and its hydrogen combining with the oxygen of the base. But this is only an assumption or possible explanation; and it does not invalidate the force of the analogy which is in favour of the other.

Are the substances formed by muriatic acid with the salifiable bases analogous to those formed by other acids? If they are compounds of it with the respective alkalis,

earths, and metallic oxides, as the old theory assumes,
they must be analogous to salts. If they contain neither
acid nor base, as the new doctrine maintains, but are com-
pounds of the metallic radicals with chlorine, they ought
to exhibit no saline properties; but as chlorine is held to
be an element analogous to oxygen, ought to be similar
to metallic oxides. They are perfectly similar, however,
to other salts. Muriate of potash, muriate of soda, and
muriate of lime are as strictly saline bodies in all their pro-
perties, as sulphate of potash, phosphate of soda, or ni-
trate of lime. Nay, with regard to some bases, muriatic
acid is held in the new doctrine to combine without de-
composition, as with ammonia, which, containing no oxy-
gen, cannot decompose it, and with alumina and magnesia,
the oxygen of which does not abstract its hydrogen, for it
is expelled from them by heat. Yet the muriates of am-
monia, alumina, and magnesia, have no saline properties
more characteristic than the muriates of potash, barytes,
or lime.

No fact has ever been produced which the old doctrine
does not perfectly explain. Oxymuriatic acid, it is said,
cannot be decomposed by charcoal, even when the action
of the latter is aided by the most intense heat. Yet as it is
supposed to be decomposed by other substances abstracting
its oxygen, it ought equally to suffer this change from
charcoal. The cause of this is very easily assigned. In
those cases, the muriatic acid either receives the portion
of water essential to its constitution in an insulated form, or
it passes into a state of combination with the substance re-
ceiving its oxygen. With charcoal neither of these can
take place; it can supply no water, so as to admit of the
muriatic acid existing in a separate state; and the substance
formed by the oxygenation of charcoal, whether carbonic
oxide or carbonic acid, has no known affinity to muriatic
acid. The attraction of charcoal to oxygen is not sufficient
to insulate the radical of muriatic acid, nor is there any

reason to believe that it should ; hence, under such conditions, the oxymuriatic acid must remain unchanged. But in the opposite doctrine, if chlorine be an element analogous to oxygen, why should it not combine with charcoal, as well as with other inflammable bodies. This is a difficulty which it will not easily explain.

It has been maintained, that the one doctrine is a theory, the other an hypothesis. There is no proof, it is said, that oxygen exists in oxymuriatic acid, or water in muriatic acid. This is merely taking for granted what is to be proved. There is a series of facts, whence the existence of oxygen in oxymuriatic acid, and of water in muriatic acid, may be inferred. The same facts may be explained in a different manner,—that the oxygen obtained is derived from the decomposition of water which is present, and that the water is formed by the hydrogen of the acid. But these conclusions are not more strictly demonstrated than the others. The whole presents a series of phenomena which are capable of being explained on both views; and which of them is to be preferred must be determined, in want of more conclusive evidence, from the consideration of which affords explanations least complicated, and conformable to the strictest analogies. In this respect every superiority belongs to the old doctrine compared with the new. The analogy of the muriatic acid to other acids in which the existence of combined water is admitted, and the analogy of the muriates to other salts, are alone sufficient to establish this.

The circumstance that the quantity of oxygen which is given out when oxymuriatic gas acts on an oxidated base, is exactly the quantity which the base contains, was regarded by Davy as a proof that it is derived from the base. This is of no weight whatever ; for from the law of equivalent quantities, the very same result must happen, supposing the oxygen to be derived from the acid.

A few analogies support the hypothesis of chlorine.

Sulphur, for instance, forms an acid by combining with hydrogen. Chlorine, therefore, considering it as a simple body, may also be supposed to form an acid in combining with the same element. But there is no analogy whatever between muriatic acid, and the acid which sulphur forms with hydrogen, while there is the closest analogy between it and the acids which contain oxygen with combined water.

The discovery of a new substance, Iodine, which has relations in several respects analogous to chlorine, gave considerable support to the new system, and chiefly contributed, as Gay-Lussac has remarked, to fix the opinion of the greater number of chemists in its favour. Yet iodine has little analogy in properties to chlorine; and were the analogy more strict than it is, it would only serve to render more probable the conclusion which some considerations suggest, that iodine is a compound, and is an oxidated body.

In relation to this question, some experimental investigations occurred to me, when it was first proposed, which promised to afford more conclusive evidence. These led to a complicated controversial discussion, to which it is now sufficient to refer *, stating only, in concluding these observations, on the comparative merits of the two doctrines, the result which is most direct, and involved in least ambiguity.

When muriatic acid gas is submitted to the action of any alkaline base, or metallic oxide, a neutral compound is formed, and a portion of water, equal to ¼th of its weight, is liberated. In conformity to the common induction from the analogous result in the action of other acids, it may be inferred, that this is water which had existed in combination with the muriatic acid. Its production, how-

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* Nicholson's Journal, vol. xxviii, xxix, xxx, xxxi, xxxii, xxxiv.

ever, may be explained in a different manner; it may be supposed to be formed by the combination of the hydrogen of the acid with the oxygen of the oxide; and, accordingly, this explanation is given in maintaining the doctrine of chlorine.

Ammonia, however, is a base containing no oxygen. If water, therefore, is obtained when muriatic acid is neutralized by ammonia, the result is incapable of being accounted for on this hypothesis, and must be admitted as a demonstration that it is derived from the muriatic acid.

To determine the fact, I combined muriatic acid and ammoniacal gases over dry mercury or in an exhausted vessel, each gas being previously exposed to the action of substances powerful in abstracting humidity, so as to be rendered free from hygrometric vapour. The salt formed was collected and exposed in a tube or small retort to a heat raised gradually to sublimation. Water was expelled and condensed in spherules at the extremity of the tube, or in the neck of the retort.

Various objections were opposed to this result. It was supposed to arise from the presence of hygrometric vapour in the gases; but this it was easy to obviate by the gases having been previously exposed to the action of substances, by which all hygrometric vapour is known to be removed from them, and by its being altogether inadequate to account for the quantity procured. It was also maintained that the salt attracts moisture from the air; and it was asserted, that when this was prevented by forming it and then applying heat, in a close vessel, not the slightest trace of water was obtained. I shewed, by diversified experiments, that the salt absorbs no moisture from the air in the common state of dryness and temperature in which the experiment is performed; it gains no weight from exposure to the air, and it remains perfectly dry; it affords, when treated in the same mode, the same portion of water, whether it has been exposed to the air in the freest manner or

not; and when heated without the air being admitted, water is obtained from it, though, from the circumstances attending this mode of conducting the experiment being unfavourable to the expulsion of the water, the quantity is rather less than what is procured in the other mode *.

The only circumstance rendering the result less decisive than it otherwise would be, is, that the quantity of water is not considerable, and is less than what is obtained by means of other combinations into which muriatic acid enters with salifiable bases. But this is to be expected from the volatility of the ammoniacal salt, in consequence of which the same degree of heat cannot be applied to it to overcome the attraction by which the water is retained.

To obviate this as far as possible, I added the experiment of subliming the muriate of ammonia through an ignited tube, either alone, or containing charcoal which had been previously thoroughly calcined. An additional quantity of water was procured by the effect of the higher temperature thus favourably applied.

Dr Ure afterwards performed the experiment, by subliming sal ammoniac over ignited metals in a tube, and with the same result of the production of water †.

I repeated this experiment, operating on the salt formed by the combination of the two gases previously carefully dried, and with a similar result ‡.

It occurred to me, that muriatic acid in its gaseous form might be employed in a similar manner. I accordingly found, in a series of experiments executed in various modes, that when muriatic acid gas, previously thoroughly dried by exposure to muriate of lime, is transmitted over ignited iron-filings, or is heated in a retort, from which the air is excluded, with iron or zinc, a portion of water is obtained.

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* Nicholson's Journal, vol. xxxii, p. 185; xxxiv, p. 264.
† Transactions of the Royal Society of Edin. vol. viii, p. 329.
‡ Ibid. p. 293.

The quantity was estimated to amount to about the fifth of the whole quantity of combined water, which muriatic acid gas is calculated to contain.

To the details of these experiments I refer *. The quantity of water is inferior to what is procured by other methods from muriatic acid gas. But it must be so. In the case of its action on metals, a portion of it must be spent in the oxidation of the metal to combine with the real acid, and it is probably only from a supermuriate being formed that any water is liberated. And in applying heat to muriate of ammonia the impossibility of applying the requisite degree, without volatilizing the salt, must prevent more than its partial liberation. But in all these forms of the experiment water is procured in quantities more considerable than what can be accounted for from any extraneous source; and this leads me to give more weight to the result †.

It was in considering this subject with more minute attention that the view occurred to me, which I have already illustrated in delivering the general doctrine of acidity, and which I have now to explain a little more fully as applied to the constitution of muriatic acid.

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* Transactions of the Royal Society of Edin. vol. viii, p. 287.

† Sir H. Davy has asserted, with regard to these last experiments, that the water is produced either from the combination of hydrogen disengaged from the muriatic acid by the metal with the oxygen of the air in the tube, or by the action of the acid on the oxide of lead and the alkali in the glass. These causes, I believe, have little or no influence on the result. The water does not appear until after the air in the tube has been entirely expelled by the muriatic acid gas. And were it even granted, that at a red heat the glass is liable to be acted on by the acid, in the greater number of the experiments I performed the heat applied was much lower, and the glass did not exhibit the slightest appearance of being acted on. The objection is not better founded than the one formerly maintained, that the water is derived by absorption from the atmosphere.

Admitting water to be procured from muriatic acid by the action of any base upon it, it does not necessarily follow, as had been presumed, that water pre-exists in the acid. It is possible that it may exist rather in the state of its elements; and that in the reciprocal action of the acid and base, these are brought into combination, so as to form the water obtained. And in all other cases in which water is procured from acids, the same conclusion may be drawn. The argument in support of this general doctrine I have sufficiently illustrated, (page 163.)

Assuming this view, muriatic acid must be regarded as a ternary compound of a radical still undiscovered, (to which from analogy the name of *Murion* may be given,) with oxygen and hydrogen. Oxymuriatic acid is a compound of the same radical with oxygen. When hydrogen is added, therefore, it is converted into muriatic acid. When muriatic, on the contrary, is converted into oxymuriatic acid, the hydrogen is abstracted by the oxygen, which effects the change; hence the production of water which accompanies it. The ultimate result of the action of muriatic and oxymuriatic acids must be the same, only accompanied in that of the former with an evolution of the hydrogen which is an element in its constitution. And in their action on oxides, the hydrogen with a corresponding portion of oxygen, in the case of muriatic acid, form water, while in that of oxymuriatic acid this proportion of oxygen is liberated.

This view appears to me superior to either of the others, in the probability of its principles, and in its adaptation to the phenomena. To support this I add a few illustrations.

Chlorine, if it is to be regarded as an element communicating acidity to hydrogen as a base, has none of the properties which would place it in the same class with oxygen. Its combining weight is high, nearly indeed at a mean among the acids. And the compounds it forms with inflammables and metals have no resemblance to those of oxygen; it does not even unite with carbon, and it forms no

acid, in the proper sense of the term, but with hydrogen, or, what is singular under this point of view, with oxygen. If, on the contrary, it is to be considered as a body acidified by hydrogen, and thus to be associated with sulphur, its want of inflammability, its being attracted to the positive electrical pole, and the nature of its compounds with inflammables and metals, render this analogy not less imperfect. All these violations of analogy are obviated, and the strictest conformity established, when it is regarded as an oxidated body ; its uninflammability and its electrical relations accord with this; it cannot be supposed to form acids in combining with other acidifiable bases; while its acidity may be expected to be exalted by the addition either of hydrogen or oxygen. Regarding it indeed as a binary acid, there is the closest analogy between it and sulphurous acid in all their essential properties,—their solubility in water, and remaining combined with it in congelation, their suffocating odour, their power of destroying colours, their inferior acidity compared with sulphuric and muriatic acids, their combining weights, and their electrical relations ;—and any peculiarity in oxymuriatic acid is evidently owing to its excess of oxygen.

The relations of muriatic acid are equally favourable to the same view. It has scarcely any resemblance to the acids which are formed by hydrogen without the presence of oxygen, sulphuretted hydrogen or prussic acid, while it has the strictest analogy to those acids which are of ternary composition, containing oxygen and hydrogen as constituent elements.

By admitting the existence of hydrogen in the composition of this acid, the doctrine has all the advantage which is claimed from the analogy of sulphur, iodine, and cyanogen being acidified by that element. And by admitting also oxygen as a constituent ingredient, there is the same advantage in being enabled to explain, from the joint operation of these elements, the higher degree of acidity be-

longing to it, which there is in applying this principle to the constitution of other binary and ternary acids formed from the same radical. While considering them, according to the old doctrine, as existing in it in the state of water, no explanation can be given of this striking result.

The same view is applied with peculiar advantage, as I shall afterwards have to illustrate, in explaining the properties of the compounds formed by the action of oxymuriatic acid on the acidifiable inflammables, 'and which are altogether anomalous on either of the other hypotheses.

It has, lastly, all the advantages of the old doctrine, in considering the muriates as saline bodies perfectly analogous to other salts. And to oppose this weight of analogy and of evidence, there remains merely the affectation of strictness of induction, in holding that every substance must be ranked as simple, the composition of which is not actually demonstrated.

Admitting this view of the constitution of muriatic acid, the proportions of its elements may be inferred from the law established by Berzelius, already stated, (vol. i, p. 155.) that the quantity of oxygen in an acid is either equal to, or is a simple multiple of the quantity of oxygen in a base which it saturates. From the degrees of oxidation in the muriatic compounds, and from the proportions in the muriates, it follows, he remarks, that the quantity of oxygen in muriatic acid is twice the quantity of oxygen in a base with which it combines. Selecting the latest, and it may be presumed the most accurate analysis of the muriates, best calculated to determine the result, such as that of potash, of silver, or of lead, it is found, that 100 parts of acid saturate a quantity of base containing 29.1838 of oxygen; they contain therefore twice that quantity, and hence muriatic acid consists of 41.632 of radical, and 58.368 of oxygen [*].

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[*] Annals of Philosophy, vol. iii, p. 54.; vii, p. 276. Annales de Chimie et Physique, t. v, p. 176.

This estimate applies, however, to what is called the real acid, or acid free from water. Taking the elements of this water into calculation, it follows, (as the quantity of it amounts to 25 in 100,) that 100 of the acid are composed of 31.224 of radical, 65.851 of oxygen, and 2.925 of hydrogen. This gives the combining quantity of the radical as 13.5, oxygen being 10 : And the proportion of oxygen is its third equivalent quantity. *Murion* is lower, therefore, in the scale of equivalents, than the other acidifiable bases ; and in the series of bodies follows oxygen.

Muriatic acid, it has been stated, is always procured from muriate of soda, (sea salt,) decomposed by sulphuric acid. It is generally under the form of its solution in water that it is employed as a chemical agent, and the process is therefore conducted so as to obtain it in this state. Two parts of the salt previously submitted to a red heat, to remove any impurities, are put into a retort, and one part of sulphuric acid is poured upon it. The sulphuric acid combines with the soda, and an effervescence takes place, from the disengagement of muriatic acid gas ; this soon ceases. The retort having been previously placed in a sand bath, and being connected with the bottles of Woulfe's apparatus containing water, heat is applied ; the muriatic acid gas continues to be disengaged, a portion is condensed in the first bottle by the water which distils over from the materials, but the greater part passes in the gaseous state into the water in the other bottles by which it is absorbed. The application of the heat is continued as long as there is any disengagement of gas. To avoid the effervescence that attends the pouring the sulphuric acid on the dried muriate of soda, it is sometimes previously diluted with half its weight of water, a method which is more convenient, and in this case more of the product is condensed in the first bottle. One part of acid to two of muriate of

soda, though the proportion generally given, is not suffi-
cient. Vauquelin recommends 3 parts to 4, which is pre-
ferable, the exact proportion of hydrosulphuric acid ne-
cessary to saturate the soda in 100 of the muriate being 84.
The process is conducted in glass vessels ; but when pre-
pared for purposes in the arts, it is sometimes done in an
iron pot to which an earthen head is adapted.   The resi-
duum is sulphate of soda, often with an excess of acid.

Even when the distillation has been carried on in glass
vessels, the acid is not perfectly pure.   It is of a yellow
colour, while pure muriatic acid gas combined with water
is colourless.   This colour has been ascribed to a little
sulphur remaining in the sulphuric acid, and brought
over by the muriatic acid gas ; to the presence of a little
oxymuriatic acid; or to extractive matter which adheres
to the muriate of soda obtained by evaporation from sea
water : this last opinion appears to be just, from the cir-
cumstance, that if the salt has been previously exposed to
a red heat, the colour is less deep.   It seems also to arise
in part from the presence of iron contained in the sea salt,
derived from the iron vessel in which the evaporation of
sea water is performed.   The acid is obtained pure by
distilling it again, a little muriate of soda having been put
with it into the retort, and water into the receivers.

Muriatic acid in its gaseous state may be obtained, by
applying to the liquid muriatic acid a moderate heat.   It
is disengaged, and as it is absorbed by water with rapi-
dity, it must be received over quicksilver.   It can equally
be procured by adding to muriate of soda half its weight
of sulphuric acid, and, after the first effervescence is over,
applying a very gentle heat, the extremity of the retort be-
ing placed under a jar inverted in the pneumatic trough
filled with quicksilver ; a large quantity of gas is disengag-
ed.   This is the process generally employed to obtain it
for experimental purposes.

Muriatic acid gas has a peculiar pungent smell; if inspired, even diluted with atmospheric air, it occasions a sense of suffocation.   When dry, it is colourless; but when presented to atmospheric air, white vapours are formed from its combination with the aqueous vapour present; hence they are more copious in a humid atmosphere. Its specific gravity was stated by Kirwan, to that of atmospheric air as 1.929 to 1000 ; and by Brisson, at 1.43 ; but this is too high.   Davy and Dalton found it to be 1.23, Biot and Gay-Lussac make it 1.27; and Biot and Arago 1.2474.   According to these latter estimates 100 cubic inches weigh 38 or 39 grains.

Muriatic gas is not inflammable; and it is incapable of supporting combustion.   A lighted taper immersed in it is extinguished, the flame first assuming a green tinge.

The relation of muriatic acid to what has been called its combined water has been explained in the preceding statement.   From the most accurate results the quantity contained in the acid gas appears to amount to one-fourth of its weight.   This was inferred by Gay-Lussac, from the quantity it deposites in combining with those bases, with which it forms insoluble compounds, as with oxide of silver.   It may also be inferred from its production in the mutual action of oxymuriatic acid and hydrogen gases. They combine in equal volumes to form muriatic acid; the oxymuriatic gas contains half its volume of oxygen, which combines with the hydrogen, and the weights of these give a quantity of water equal to 0.245 of the acid gas which is produced *.   The acid cannot be obtained free from any portion of this water in an insulated state; and, according to the view I have stated, the elements of the water exist in its composition, forming a ternary acid. In the decomposition of the acid by the action of a salifiable base, its hydrogen combines with the corresponding

* Mémoires d'Arcueil, tom. ii, p. 339.

portion of oxygen, forming the water which is deposited, or, when it acts on metals, the oxygen is retained, and the hydrogen is liberated. Electricity evolves a portion of hydrogen and of oxymuriatic gas, but to this there is a limit, as Dr Henry has shewn, by the electric spark favouring their re-combination when they are accumulated in a certain proportion *. No hygrometric vapour appears to exist in this gas. Dr Henry found, that it deposites no trace whatever of moisture when intensely cooled. Gay-Lussac and Thenard obtained the same result, and found also, that fluo-boric gas, which, by the opacity it produces when aqueous vapour is present, discovers it with the greatest delicacy, did not in the slightest degree affect the transparency of muriatic acid gas; and, conversely, when the gas had been dried by exposure to muriate of lime, a drop of water introduced into it, instead of diminishing by evaporation, increased in volume †.

The attraction of muriatic acid gas to water is strong; it combines with it with great rapidity, and is condensed in very large quantity, the water taking up about 500 times its volume of the gas. Its bulk is by this absorption increased about one-third, and its weight doubled. The absorption is attended with the production of heat. Ice is instantly melted in the gas, and the temperature falls,— a fact which proves that the liquefaction of a solid may absorb more caloric, than the condensation of a gas into the liquid state gives out. The specific gravity of the liquid in the state of concentration in which it is obtained by the process of the Edinburgh Pharmacopoeia, is 1.170; but in commerce it is often not more than 1.155. The strongest that can be procured is that of 1.2 at 50°. The following table, by Mr E. Davy, shews the quantity of muriatic acid gas contained in the liquid acid at different

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* Philosophical Transactions, 1812.
† Recherches Physico-Chimiques, tom. ii, p. 73.

degrees of specific gravity. A table was given by Kir-
wan, and corrected by Dalton*, of the quantity of real
acid, as it is called, in acids of different specific gravities;
but it does not correspond with that of Davy's, and there
is reason to believe is not correct in the estimation of acid.

TEMPERATURE 45°, BAROMETER 30.

Specific gravity.	100 grains contain of muriatic acid gas.	Specific gravity.	100 grains contain of muriatic acid gas.
1.21	42.43	1.10	20.20
1.20	40.80	1.09	18.18
1.19	38.38	1.08	16.16
1.18	36.36	1.07	14.14
1.17	34.34	1.06	12.12
1.16	32.32	1.05	10.10
1.15	30.30	1.04	8.08
1.14	28.28	1.03	6.06
1.13	26.26	1.02	4.04
1.12	24.24	1.01	2.02
1.11	22.3		

The muriatic acid of commerce, though not saturated
with the gas, is strongly acid. A drop of it reddens the
vegetable colours; it is corrosive, and, even largely dilu-
ted, tastes extremely sour. It exhales vapours, of a pun-
gent suffocating odour, when presented to the atmosphe-
ric air, from the escape of part of the muriatic acid gas,
which combines with the vapour of the atmosphere.

As it is incapable of affording oxygen, it does not act
with much energy on the metals; and charcoal, sulphur,
and phosphorus, are scarcely affected by it. By a dispos-
ing affinity, however, it enables a number of the metals to
decompose the water present and receive the oxygen; it
thus dissolves them, those especially which exert a strong
attraction to oxygen, as iron or zinc, the solution being
attended with the extrication of hydrogen gas. It also ex-
erts a strong affinity to metallic oxides, and decomposes

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* System of Chemical Philosophy, p. 295.

many of their combinations with the other acids.   Its most
delicate test, and that which discovers it in all its combi-
nations, is derived from the affinity it exerts to oxide of
silver, with which it forms a dense precipitate, so that a
few drops of nitrate of silver added to any liquid contain-
ing the smallest proportion of muriatic acid, gives rise to
a cloudiness from the production of this insoluble com-
pound.   The acid in its gaseous state likewise acts on
those metals which have a strong attraction to oxygen, as
iron or zinc, and also on potassium and sodium.   Hydro-
gen is evolved, and dry muriates are formed ; results
which, it has been already stated, are on the one doctrine
considered as arising from the decomposition of the acid,
and on the other from the decomposition of the water
which the acid contains, the metal attracting its oxygen,
and the oxide combining with the real acid.   The result,
according to the view I have illustrated, is probably a
ternary compound of the radical of the acid and the metal
with oxygen.

This acid combines with the alkalis and earths, forming
salts named Muriates.   Their taste is that termed pecu-
liarly saline ; they are soluble and crystallizable ; they are
not decomposed by heat, at least this is the case with the
alkaline muriates ; they are partially decomposed by the
sulphuric and by other acids ; and if heat be applied to
favour the elasticity of the muriatic acid, the decomposi-
tion is complete, when that quantity of water is supplied,
the elements of which the muriatic acid gas requires.   If
this is not present, the muriatic acid is not expelled even
at the most intense heat, as has been already stated.   They
are also decomposed by some of the earths which exert an
attraction to the base, as by alumina or silica at a high
temperature, and these decompositions are equally aided
by the presence of water.   When perfectly freed from wa-
ter by the heat of ignition, they are regarded, on one hy-
pothesis, not as neutral salts, but as analogous to oxides,

—compounds of chlorine and metallic bases. The esti-
mate of their composition, on this view, may be converted
into the corresponding results, according to the opposite
doctrine, by considering them as dry muriates, and find-
ing the proportions of oxygen and acid according to the
known proportions of these in oxymuriatic acid ; and con-
versely, their composition as chlorides may be inferred
from their proportions as muriates. Their composition is
usually determined by precipitation by nitrate of silver ;
the muriatic acid, according to the one hypothesis, or the
chlorine, according to the other, being abstracted from the
base, and transferred to the silver or oxide of silver ; and
the precipitate, (which is perfectly insoluble,) being wash-
ed and dried at a red heat, 100 parts of it, according to
the one view, represent 19.05 of dry muriatic acid, and,
according to the other, 24.5 of chlorine.

From the hypothesis of chlorine and hydrogen being the
elements of this acid, Gay-Lussac has given it the name
of Hydro-chloric, and its salts he names Hydro-chlorates,
an innovation without any advantage, and improper as in-
troducing theoretical terms.

Sect. III.—*Of Oxymuriatic Acid.*

THE substance to which this name is applied was con-
sidered as a compound of muriatic acid and oxygen, from
being formed when oxygen is communicated to that acid,
and returning to the state of muriatic acid when oxygen
is abstracted. In these cases of its formation and decom-
position, Gay-Lussac and Thenard observed, that water
has an important influence, a quantity of it being produ-
ced in those processes in which oxymuriatic acid is form-
ed, and a quantity of it being required to admit of the
change into muriatic acid. The theory of these facts, and

of the constitution of oxymuriatic acid connected with them, has been illustrated in the preceding section.

Scheele, it has been stated, discovered this substance. It is not easily formed by the combination of muriatic acid and oxygen in their gaseous form. But by presenting them in a nascent state, they unite; and it was by a process of this kind that Scheele effected their combination, and discovered the acid. In investigating the nature of the black ore (or native black oxide) of manganese, he observed, that in dissolving it in muriatic acid a vapour was disengaged, of a yellow colour, and of a peculiar suffocating odour; and in the investigation which this observation led to, he found, that by distilling the muriatic acid from this ore, an aerial fluid was obtained, having qualities altogether different from those of muriatic acid. Several of these he pointed out, particularly its more sparing solubility in water, its inferior acid power, its peculiar energy in destroying the vegetable colours, and its power of dissolving the greater number of the metals. From the change which he found to be effected in the oxide, or calx of manganese, he inferred, in conformity to the theoretical opinions then received, that the muriatic acid was deprived of phlogiston; and hence he gave to this new product the name of Dephlogisticated Marine or Muriatic Acid *. This required, in the general theory of Lavoisier, advanced soon after this time, a change of terms merely to represent it as Oxygenated Muriatic Acid. Berthollet pointed this out, and gave it this appellation, which was abbreviated afterwards into Oxymuriatic Acid. He, at the same time, shewed more clearly, that the native oxide of manganese loses oxygen in converting the muriatic into oxymuriatic acid, a synthetic proof apparently of the composition of the latter; and he added the elegant analytic experiment of exposing a solution of oxymuriatic gas in

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* Chemical Essays, p. 90.

water to the rays of the sun ; it returned to the state of muriatic acid, and pure oxygen gas was obtained *. When the doctrine had been advanced, that it is a simple substance without acidity, Sir H. Davy gave it, from its characteristic yellowish green colour, the name of Chlorine. The term Oxymuriatic acid is not strictly correct, according to the theory of its constitution which I have proposed, for it does not differ from muriatic acid merely in oxygenation, nor does it even contain a larger proportion of oxygen. But, in the present state of chemical nomenclature, there would be some difficulty, and little advantage in introducing another name.

Berthollet inferred the composition of oxymuriatic acid from the quantity of oxygen obtained when its watery solution is exposed to the solar rays, and the quantity of muriatic acid which remains as estimated by precipitation by nitrate of silver : the proportions, he assigned, were 89 of acid and 11 of oxygen. But the quantity of oxygen is stated too low. Chenevix attempted its analysis in another mode. When oxymuriatic acid acts on solution of potash, part of it returns to the state of muriatic acid, by yielding oxygen to the other portion, which thus becomes an acid with a large proportion of oxygen, and each of these combines with the alkali to neutralization. He found the quantity of muriatic acid in each salt, and the quantity of oxygen which the oxygenated salt gives out when decomposed by heat : and from this he inferred, that the proportions in the oxymuriatic are 84 of muriatic acid, and 16 of oxygen ; and Berthollet, correcting his results by an alteration in the estimate of the muriatic acid in muriate of silver, obtained nearly the same proportions †. The proportion of oxygen appears, however, to be still too low. Gay-Lussac found from experiment the proportions

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* Mémoires de l'Acad. des Sciences, 1785, p. 276.
† Chemical Statics, vol. ii, p. 169.

to be 22.92 with 77.08 of acid *.   Dalton assigned them
also from experiment very nearly the same †.   And Dr
Wollaston gives the estimate of 77.32 of acid, and 22.68
of oxygen.   Converting the proportions which Gay-Lus-
sac gives into those by volume, they give 300 of muriatic
acid gas, and 103.2 of oxygen gas, proportions which dif-
fer little from those of 3 to 1, and which accord therefore
with his view of elastic fluids combining in simple propor-
tions by volume.   In this estimate, however, muriatic acid
gas contains 0.25 of water, while in the estimate by weight
it is the real acid that is calculated on.   It follows from
this, as Gay-Lussac remarks, that water in its combina-
tion with dry muriatic acid to form common muriatic acid
gas, does not sensibly change its specific gravity.   Oxy-
muriatic gas consuming exactly an equal volume of hydro-
gen in their mutual action, and two measures of hydrogen
gas condensing exactly one measure of oxygen gas, it fol-
lows that oxymuriatic acid gas contains just half its vo-
lume of oxygen gas.

On the view which I have stated of the constitution of
muriatic and oxymuriatic acids, the proportion of oxygen
to that of the radical in each is the same, and the former
differs from the latter only in containing a certain propor-
tion of hydrogen.   Admitting the proportions which were
assigned to muriatic acid, (p. 433.), the proportions in
oxymuriatic acid will be 32.164 of radical, with 67.836 of
oxygen.

Oxymuriatic acid is usually obtained by the process de-
scribed by Scheele; distilling diluted muriatic acid from
one-fourth of its weight of black oxide of manganese.   It
is more economical to employ the materials from which
muriatic acid is obtained.   Four parts of muriate of soda
are mixed with rather more than one part of black oxide

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* Mémoires d'Arcueil, tom. ii, p. 217.
† Chemical Philosophy, p. 302.

of manganese in powder; the mixture is put into a retort, and there are poured upon it three parts of sulphuric acid previously diluted with two of water. An effervescence takes place, and the upper part of the retort becomes tinged of a yellowish green colour. On applying heat, oxymuriatic gas is abundantly formed and disengaged. If it is designed to obtain it in combination with water, the retort is placed in a water-bath, and connected with the bottles of Woulfe's apparatus, in which water is placed; what condenses in the first bottle is not pure oxymuriatic acid, but consists partly of muriatic acid, holding dissolved a little oxide of manganese; the pure gas passes into the other bottles, and absorbed by the water affords the liquid oxymuriatic acid. The apparatus of Dr De Butts, described vol. i, p. 291, is peculiarly adapted to this distillation, as confining more effectually the oxymuriatic gas, which from its suffocating operation is extremely injurious. If the object be to obtain the acid in its elastic form, heat is applied by the medium of a lamp or taper, and the gas is received over water, the temperature of which is about 90°, as at this temperature it absorbs scarcely any of it, and quicksilver is not only inconvenient, but is acted on by the oxymuriatic gas.

In this process the sulphuric acid combines with the soda of the muriate of soda, and disengages the muriatic acid, and this acid receives oxygen from the black oxide of manganese, and is thus converted into the oxymuriatic. At the end of the process, the black oxide of manganese is found deprived of much of its oxygen, or is reduced from the *maximum* to nearly the *minimum* of oxidation. With this imperfect oxide of manganese, a portion of the muriatic acid remains combined, forming a muriate of manganese mixed with the sulphate of soda. Some other metallic oxides, particularly oxide of lead, may be employed: and according to Mr Dalton's experiments, oxymuriatic gas

is formed by direct combination, by transmitting electric sparks through a mixture of muriatic acid gas and oxygen gas. Water is deposited in its formation by passing muriatic acid gas over oxide of manganese heated ; and there must be a similar result in the other processes. The theory of this according to the different views is sufficiently evident.

Oxymuriatic acid is gaseous under a common atmospheric pressure ; by great pressure Mr Northmore succeeded in condensing it into a liquid *, probably, however, by the agency partly of vapour in the gas. It is heavier than atmospheric air ; its specific gravity Dalton found to be 2.34 ; but this is probably rather low : Gay-Lussac and Thenard found it to be 2.47, and Davy states it at 2.44. 100 cubic inches weigh according to the former 76.5 grains ; according to the latter, 75.5 grains. The gas has a yellowish-green colour, and is one of the few elastic fluids distinguished by colour. Of all the gases it is the most insupportable in its action on the lungs. When pure, it occasions immediate death if an animal is immersed in it ; and even when largely diluted with atmospheric air, it cannot be respired with safety ; it occasions a severe sense of stricture at the breast, which renders it impossible to make a full inspiration ; this continues for a considerable time after it has been inspired : and has often produced a permanently injurious effect.

Oxymuriatic gas is not decomposed by heat ; from its watery solution it rises unchanged ; and according to Gay-Lussac and Thenard, when dry, it passes through a red-hot tube without any change. But if humid, it suffers decomposition ; and if the vapour of water be passed through the tube with it, a large quantity of oxygen and muriatic acid gas is obtained. This happens even at a temperature

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* Nicholson's Journal, vol. xiii, p. 134.

below ignition *. The electric spark has no sensible effect on it.

A similar effect is produced by light as by heat. The acid in its gaseous state, Fourcroy remarked, is not decomposed by exposure to the solar rays; while its watery solution is decomposed with great facility, and oxygen gas is disengaged.

Oxymuriatic gas is absorbed by water, the quantity being larger as the temperature is low. At 50° the water appears to take up about twice its volume. In this absorption a singular phenomenon occurs when the temperature is below 40°. As the water becomes saturated with the gas, small soft scales form in the liquid, which increase as the absorption proceeds, inclosing the fluid part until the whole become of a gelatinous appearance, or even congealed; and, under favourable circumstances, regular crystals of the figure of a quadrangular prism are formed. This concrete matter melts on the application of a moderate heat, and the gas rises in bubbles through the liquid. It is the combination of the oxymuriatic acid with water. The gas itself, when obtained dry, is incondensible by cold; but if transmitted through water, so as to be saturated with it, it is condensed by a low temperature. The fact of this crystallization is a singular one, and it is rendered more so by another, that the gas, in combining with water, does not part with much caloric, as the temperature is scarcely sensibly raised, nor is the liquid much heavier than water,—a proof that it has not experienced a great condensation from the combination.

The saturated solution of oxymuriatic gas in water has a yellowish-green colour; it has the intolerable odour of the gas; the taste is not sour, but harsh and styptic, and it does not redden, but destroys the vegetable colours.

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* Mémoires d'Arcueil, t. ii, p. 346. Recherches Physico-Chimiques, t. ii, p. 144.

From having no sour taste, and from not reddening the vegetable colours, the acidity of this substance may be called in question. Sourness of taste, however, may be prevented by a more pungent sensation, and accordingly, it is not to be perceived in sulphuretted hydrogen, scarcely in sulphurous acid when it is pure, and perhaps not perceptibly in some of the metallic acids, and in certain acidulous salts. The reddening effect is of course prevented, when the agency exerted is that of destroying colour; and this is to a certain extent apparent likewise in the action of sulphurous acid. The acidity of oxymuriatic acid is established by the most characteristic of all acid properties, that of combining with alkaline bases, neutralizing their properties, and by equivalent proportions exchanging, in these combinations, bases with other saline compounds.

Oxymuriatic gas acts with much energy on inflammable and metallic bodies. It was early observed that a lighted taper immersed in it is not immediately extinguished, but burns with a dense flame: And it was found, that a number of inflammable substances suspended in it at a temperature of 60° or 70° take fire and burn. Phosphorus inflames and burns with splendour. A number of the metals, and their combinations with sulphur, exhibit similar phenomena. Antimony, arsenic, bismuth. zinc, copper, and sulphurets of antimony, and mercury, either in filings or powder, projected into the gas take fire ; the combustion of some of them, as antimony or arsenic, is even brilliant, and is marked with peculiar coloured flame. For the success of these experiments, it is necessary that the gas should be pure, and that the temperature should not be lower than 70° *. Potassium burns spontaneously in this gas, and the combustion is vivid when heat is applied. Sodium does not inflame unless it is heated.

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* Crell's Chemical Journal, vol. i, p. 137.

The products of these combinations are considered in the old doctrine as compounds of muriatic acid with oxidated bases, the inflammable or metal receiving oxygen from the oxymuriatic acid, and the oxide combining with the real acid. According to the view I have proposed, they are probably ternary compounds of the radical of the acid, the metal or inflammable, and oxygen. Considering chlorine as a simple body, they must be considered as compounds of it with the inflammable or metal. On this last assumption different systems of nomenclature have been applied to denote them. Sir H. Davy proposed to derive the name from the Latin name of the base, and to indicate the difference of proportion by a variation in termination, the terminating syllable being *ane* to denote the lower proportion, and *ana* to denote the higher, as, for example, cuprane, cuprana, applied to denote the two compounds of copper with chlorine, phosphorane and phosphorana the two combinations of phosphorus, &c. This nomenclature is at variance with all the analogies of chemical nomenclature, and has not been adopted. It has been proposed to apply the term Chloride to the generic name; and the compounds in the different proportions may be denoted by the terms proto-chloride, deutro-cloride, &c.: this is much preferable. Gay-Lussac has named them Chlorurets; but this term is objectionable, as the syllable *uret* is applied to the combinations of inflammable substances with each other, and chlorine has no inflammability. Those of them which are of a saline nature are distinguished, according to the old doctrine, merely as muriates in different degrees of oxidation.

If the electric spark be transmitted through a mixture of hydrogen and oxymuriatic gases, it is inflamed with detonation: and from the observation of Gay-Lussac, a temperature inferior to that of ignition is sufficient; inflammation being produced if a wire of iron heated to 334° be plunged into the mixture. Exposure to solar light has the

same effect, as Dalton and Gay-Lussac discovered. If the mixture of the two gases be exposed to the rays of the sun, it inflames immediately with detonation ; and even diffused light produces a mutual action more or less rapidly according to its intensity. If while the action is going on, the light be intercepted, it immediately ceases; and if the mixture be placed in darkness, the colour of the gas remains unchanged after a number of days, and the action is not complete in several weeks *. In all these cases muriatic acid gas is the product ; the proportions from which this result is obtained are as nearly as can be estimated equal volumes : a slight condensation attends their mutual action, but this is less as the gases are dry, and is therefore probably owing to the presence of humidity. The theory of this experiment has been already given.

A singular product is obtained by the action of oxymuriatic acid on ammonia, which has been considered as a compound of chlorine andn itrogen, and which exceeds all other substances in detonating power. It was discovered by Dulong †. Sir H. Davy also formed it without any knowledge of Dulong's method ‡. And a very extensive series of experiments was made upon it by Messrs Porret, Wilson and Kirk §. To obtain it, a small jar is filled with pure oxymuriatic gas, and is transferred into a bason containing a solution of nitrate or muriate of ammonia a little warm ; the gas is slowly condensed, and the liquor rises in the jar ; an oily-like film forms on its surface, which increases and collects into globules, which at length fall through the liquor : this is the explosive compound. Its colour is yellowish : its specific gravity seems

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* Chemical Philosophy, p. 300. Mém. d'Arcueil, t. ii, p. 349.
    † Annales de Chimie, t. lxxxvi, p. 37.
    ‡ Philosophical Transactions, 1813.
    § Nicholson's Journal, vol. xxxiv, p. 180.

to be about 1.6 ; it evaporates speedily under exposure to
the air, with a peculiar and very penetrating odour ; in
vacuo it assumes the elastic form at natural temperatures ;
it distils in close vessels at 160°, and does not freeze at
—16° ; it does not explode at 200°, but explodes violently
at 212°. The most violent explosions, however, are pro-
duced from it when it is touched cold with inflammable
bodies : a portion of it, for example, the size of a pin-head,
being brought in contact with olive oil, the vessel is bro-
ken into fragments by the violence of the explosion ; its
effects are indeed so violent, as to have given rise to severe
accidents ; hence the propriety of the precaution of wear-
ing a mask, of operating only on very small quantities, and
of taking care that the vessel in which it is formed, or the
instrument by which it is removed, shall be perfectly clean
and free from combustible matter. It is singular, that a
number of inflammable substances do not cause it to ex-
plode, such as charcoal, alkohol, or ether ; and among the
inflammable substances which either do, or do not cause it
to explode, it does not appear that any analogy can be
traced. Nitrogen gas is given out in these explosions ; it
gives the same gas from the action of muriatic acid, and
with quicksilver it forms muriate of mercury, and affords
nitrogen. Dulong found, that when decomposed by cop-
per, nitrogen gas is disengaged, and muriate of copper is
formed ; whence it follows that it is a compound of oxymu-
riatic acid and nitrogen. Sir H. Davy also, from some
of these results, considered it as a compound of chlorine
and nitrogen, composed of 91 of the former, and 9 of the
latter. From analytic experiments, Messrs Porret, Wil-
son and Kirk conclude, that it consists of chlorine, nitro-
gen and hydrogen : the hydrogen, they suppose, by its
affinities to the other elements, serves as the medium of
union ; and the great explosive power of the compound
they conceive owing to the action of chlorine condensed in
the combination, but at the same time retained only by a

weak affinity. On the admission of Sir H Davy's analysis, Berzelius supposed it to be a compound of muriatic and nitric acids free from water. It may be regarded on the same admission as a ternary compound of murion, oxygen and nitrogen.

Charcoal when perfectly freed from hydrogen by calcination is not in the slightest degree affected by oxymuriatic gas, aided even by the most intense heat,—a singular result, and presenting an anomaly; for whether chlorine be regarded as an element belonging to the same class as oxygen, or associated with sulphur, it might be expected to combine with carbon in common with other inflammable bodies; and even on the view that it is a compound of an inflammable radical with oxygen, it might be expected that a ternary combination would be established.

It has been affirmed, however, that the combination may be effected by the medium of oxygen. Cruickshank observed, that while the different varieties of carburetted hydrogen inflamed with oxymuriatic gas, from the agency of the electric spark, carbonic oxide gas did not. If a little water was admitted to the mixture of oxymuriatic gas and carbonic oxide gas, they were slowly converted into carbonic and muriatic acids, the water essential to the constitution of the latter, according to the old theory, being supplied. But when the two gases are pure and perfectly dry, they do not suffer this change. And in employing this as a form of experiment to prove the presence of oxygen in oxymuriatic acid, when the new doctrine was first proposed, I found that the green tint of the oxymuriatic gas remained evident after a number of hours, and on admitting water to condense it, the carbonic oxide was found with scarcely a trace of carbonic acid *. Gay-Lussac and Thenard also had found, that the mixture of the two gases exposed even to a strong light remained un-

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* Nicholson's Journal, vol. xxviii, xxix, xxx, &c.

changed *. Sir H. Davy had stated a similar result. According to experiments, however, brought forward at that time by Mr J. Davy, they combine together, and form a peculiar compound in the elastic form, to which, as it is produced only when they are submitted to the agency of light, he gave the name of Phosgene Gas; and the properties of which he described †. It has a penetrating odour different from that of chlorine, but still more intolerable; its specific gravity he states at 3.474, atmospheric air being one, hence it is one of the heaviest elastic fluids; it reddens litmus paper; condenses four times its volume of ammoniacal gas, forming a neutral salt which is decomposed by liquid muriatic, nitric, sulphuric and phosphoric acids, affording carbonic and muriatic acid gases, but dissolves without effervescence in acetic acid. The gas is decomposed when heated with metals, carbonic oxide being obtained, and the products which the same metals form with chlorine. It is also decomposed by water, being converted into carbonic and muriatic acids. Dr J. Davy regards it as a compound of chlorine and carbonic oxide in equal volumes, condensed by their combination into half their volume. According to the common theory, it would fall to be considered as a compound of real muriatic and carbonic acids: Or, according to the other view, as a ternary compound of the radicals of these acids with oxygen. There remain, however, some doubts with regard to it. Independent of the discordant results obtained in the experiment of the mutual action of the two gases under the influence of light, the circumstance that they do not act on each other under the agency of the electric spark, leaves room for the conjecture, that the gradual effect produced in the former case depends on some external condition, to the operation of which that mode

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* Recherches Physico-Chimiques, t. ii, p. 150.
† Philosophical Transactions, 1812.

of experiment is favourable, probably the presence of a small portion of hydrogen, or of moisture, the entire abstraction of which from the two gases is not very easily attained.

Carbon seems also to be capable of combining with oxymuriatic acid, or its elements, by the medium of hydrogen. Some of the carburetted hydrogen gases are decomposed by it, as Cruickshank shewed [*]. They detonate when the electric spark is sent through the mixture; muriatic acid, with carbonic oxide or acid are formed, in some of them also with a deposition of charcoal. But with the super-carburetted hydrogen or olefiant gas the effect is more peculiar, as was first observed by the associated Dutch chemists, in their experiments on this gas [†]. If equal volumes of the two gases are mixed over water, a condensation takes place quickly, and an oily-like matter collects on the sides of the vessel, and on the surface of the water. If four parts of the oxymuriatic gas and three of the inflammable gas be mixed together, the condensation is complete with the formation of the same product.

The oily-like matter formed by the action of these gases is whitish and semi-transparent, has a perceptible smell, which is not disagreeable, and a sweetish taste. Its specific gravity is 1.22; hence it sinks in water, but by agitation is dissolved. The solution, Dr Thomson, who made some experiments on this substance [‡], states is colourless, has a sweet taste and an aromatic odour, does not affect vegetable blues, but precipitates nitrate of silver. Alkohol and sulphuric ether, he adds, dissolve this substance; oil of turpentine does not: nitric acid dissolves it without effervescence or any sensible change: it effervesces with sulphuric acid, and a smell of oxymuriatic gas becomes sensible;

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[*] Nicholson's Journal, 4to, vol. v, p. 202.

[†] Ibid. 4to, vol. i, p. 44.

[‡] Memoirs of the Wernerian Society, vol.; p. 516.

it evaporates entirely in the atmosphere, and boils at 152. The density of its vapour is 3.4434. It burns with a green flame, with much smoke and a deposition of charcoal. It is composed, according to its analysis by Robiquet and Colin, of one volume of chlorine and one volume of olefiant gas, condensed into one volume *. But in what state the elements exist, may be represented differently according to different views.

Sulphur does not inflame in oxymuriatic gas even when heated in it; but rises in vapour and condenses, forming a reddish coloured liquid. Dr Thomson observed, that on passing a current of oxymuriatic gas through sulphur in powder, the gas is absorbed, and a liquid of a bright red colour is formed, the weight of which is more than twice that of the sulphur; its specific gravity he found to be 1.623; it is volatile, and exhales a vapour when exposed to the air, which has a pungent smell; it is decomposed by water, a little sulphur being deposited; it is also decomposed by the acids, and effervesces strongly with the alkalis. He regarded it as a compound of oxide of sulphur and muriatic acid, and named it Sulphuretted Muriatic Acid †. It was submitted to farther investigation by the younger Berthollet ‡, who considered it as a compound of sulphur, oxygen, and muriatic acid. The usual powers of the oxymuriatic acid he found to be completely suspended; but it had sensible acidity, and even the vapour arising from it reddened litmus paper. This must be ascribed, however, to the presence of humidity. Davy found that it does not redden perfectly dry litmus paper §. He finds that 10 grains of sulphur absorb about 30 cubic inches of chlorine gas. Considering the compound, there-

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* Annales de Chimie et Physique, tom. i.   Annals of Philosophy, vol. ix, p. 26.

† Nicholson's Journal, vol. vi, p. 104.

‡ Mémoires d'Arcueil, tom. i, p. 161.

§ Elements of Chemical Philosophy, p. 279.

fore, as chloride of sulphur, it is composed of 10 of sulphur and 22.8 of chlorine.

Sulphuretted hydrogen is decomposed by oxymuriatic gas. If the gases are dry, this is attended with inflammation, but in mixing them over water this is not observed. I have found, however, that if the oxymuriatic gas be allowed to escape from the end of a retort into the sulphuretted hydrogen gas, each bubble of gas, as it breaks, produces inflammation, an effect apparently owing to the density of the gas favouring its action, for with the opposite arrangement of allowing the sulphuretted hydrogen to escape into the oxymuriatic gas, there is no inflammation *. The results of the action of these gases are different according to the proportions. When they are mixed in equal volumes, and water is excluded, the whole or the greater part of the sulphur is deposited, and the hydrogen and oxymuriatic gases form muriatic acid gas. When three measures of oxymuriatic gas to one of sulphuretted hydrogen are mixed in an exhausted flask, there is no deposition of sulphur, and the transparency, which is at first impaired by a whitish vapour, is soon restored. On admitting water there is an instantaneous and nearly total absorption, and the liquid contains sulphuric and muriatic acids.

Phosphorus acted on by oxymuriatic acid affords results somewhat analogous. It inflames in the gas; and the product was supposed to be phosphorous or phosphoric acid. But Gay-Lussac and Thenard found it to be similar to a liquid which they had previously discovered, formed when muriate of mercury is heated with phosphorus, and which they considered as a ternary compound of muriatic acid, oxygen and phosphorus. This liquor is white, limpid, highly fuming, acid, and extremely caustic: paper which has imbibed it inflames on exposure to the air; it does not

* Nicholson's Journal, vol. xxviii. p. 150.

decompose when the air is excluded; but when it is ad-
mitted, it suffers decomposition in a few days, and depo-
sites a large quantity of phosphorus. It is partly dissolved
by water, and partly decomposed, phosphorus being pre-
cipitated *. Sir H. Davy observed, that in the combus-
tion of phosphorus in chlorine gas, two products are
formed, a white sublimate is condensed in the upper part
of the vessel, and a limpid fluid trickles down its sides.
The latter appears to be analogous to the compound ob-
served by Gay Lussac and Thenard. In the former, the
phosphorus appears to have condensed more chlorine.
It is very volatile, rising in vapour at a temperature low-
er than 212°; it may be melted under pressure, and on
cooling it crystallizes in transparent prisms. It reddens
litmus, and is resolved by water into phosphoric and muria-
tic acids. Its most singular property is that of combin-
ing with ammonia, and forming a compound insoluble in
water, and similar in characters to an earth. It inflames
when exposed to a lighted taper, and when transmitted
through a red hot tube with oxygen is decomposed, phos-
phoric acid is formed, and chlorine disengaged. These
two compounds were named by Sir H. Davy Phosphorana,
and Phosphorane. The first, or solid product, consists,
according to his experiments, of 10 of phosphorus and
67 of chlorine; the second of 10 of the former and 33.5
of the latter.

Phosphuretted hydrogen inflames on being presented to
oxymuriatic gas, presenting a brilliant green light; mu-
riatic acid gas is formed, and a brown or reddish-coloured
substance is thrown down. Subphosphuretted hydrogen
gas likewise inflames spontaneously in oxymuriatic gas with
a similar result, when the due proportion of the gases is
observed †.

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* Recherches Physico-Chimiques, tom. ii, p. 176.
† Davy, Philosophical Transactions, 1812.

The properties of the compounds formed by the action of oxymuriatic gas on sulphur and phosphorus do not accord well either with the old or the new doctrine on the nature of that body. According to the former, the oxygen is transferred to the sulphur or the phosphorus, and the products are compounds in the one case of dry muriatic with dry sulphuric or sulphurous acid, in the other of dry muriatic with dry phosphorous or phosphoric acid. Yet they have no properties such as might be expected from such a combination; they have in general no acidity, and even no great energy of chemical action. On the other hypothesis, chlorine is considered as a body belonging to the same class with oxygen, communicating acidity, and doing so in the example of its combination with hydrogen in a high degree. Its not giving acidity, therefore, to sulphur and phosphorus, presents an anomaly as great as on the other system. In the doctrine I have stated, these substances are regarded as ternary compounds of the inflammable substance, the phosphorus or sulphur, with the radical of the acid and its oxygen; the proportion of oxygen is not capable of acidifying both; but when water is added, an additional portion is communicated, and the corresponding portion of hydrogen likewise exerts its acidifying influence; hence a high degree of acidity is produced.

Boron was found by Gay-Lussac and Thenard not to burn in dry oxymuriatic gas. According to Sir H. Davy, when heated in it, it emits white fumes, but without any energetic action.

The general nature of the action of oxymuriatic acid on the metals has been already stated. It is condensed by them in various quantities, and products are formed, some solid, others liquid, and generally of considerable specific gravity. These, according to the common opinion, are dry muriates, the metal receiving the oxygen of the oxymuriatic acid, and the oxide thus formed combining with

the real acid. According to the opposite opinion, they are chlorides, or compounds of the metals with chlorine. By water they are converted into muriates in the common state, and are frequently at the same time decomposed, submuriates being precipitated. Their individual history belongs to their respective bases.

When oxymuriatic acid is combined with water, its action on inflammable substances is less energetic. It slowly oxidates phosphorus; on sulphur in its usual state of aggregation it scarcely acts. It is rather more active with regard to the metals; it oxidates them, and the metallic oxide remains in combination with the muriatic acid; those metals even which attract oxygen least powerfully, as gold, are oxidated and dissolved by the acid.

One of the most important properties of oxymuriatic acid is that of destroying vegetable colours. It is displayed by it either in its gaseous form, or combined with water. If the gas be transmitted through any vegetable infusion of a purple, red, or green colour, or if any vegetable coloured matter be exposed to it, the colour is discharged, or, if it has been a deep and permanent colour, becomes of a faint yellow. The same effect is produced on adding the solution of the oxymuriatic acid in water.

This effect probably depends on the communication of oxygen. This element appears to have the power of destroying the colour of vegetables, as is shewn in the effect of etiolation in vegetables in which oxygen is accumulated in the plant, and also in the old method of bleaching by air and water. And the oxymuriatic acid, in this operation of it, is found to return to the state of muriatic acid, which proves the abstraction of oxygen. The presence of water at the same time appears to be necessary to this, obviously by the affinity it exerts to the muriatic acid. Davy accordingly states, that when dry and warm litmus paper is introduced into a glass globe containing oxymuriatic gas, exposed to muriate of lime, it suffers no change of colour:

but when humidity is present either in the paper or gas the colour is discharged. According to his hypothesis, the communication of oxygen is from the decomposition of water by the oxymuriatic acid.

On this property is founded the application of oxymuriatic acid to the art of bleaching linen and cotton, an application from which important advantages are derived, the new process being performed with much celerity, saving therefore capital, being attended with less labour, and being capable of being executed in all situations, and at all seasons of the year, while, if properly managed, the texture of the thread or cloth sustains no injury. To Berthollet we are indebted for what may justly be termed a new chemical art *, since he first applied the agency of the oxymuriatic acid to this purpose. The process has undergone, however, various improvements.

The art of bleaching consists, not only in discharging the colour of the thread, but likewise in removing the colouring matter itself, as otherwise a sensible shade would be regained. In the old method, this was attained by exposure of the thread or cloth to the action of light, air and water, and alternating with this, to the action of an alkaline ley, the cloth being macerated in a solution of potash, exposed on the field to the air and sun, and frequently sprinkled with water, and these alternate practices being continued until the bleaching was complete.

In the new method, the action of the oxymuriatic acid is substituted for that of the light, air, and water; and it produces the same effect, by affording oxygen to the colouring matter, thus impairing the colour, and probably rendering the matter soluble in the alkaline solution.

At first this was done by exposing the cloth to the action of the gaseous acid ; but this was found to act unequal-

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* Annales de Chimie, tom. ii, p. 151, tom. vi, p. 204, or Translation of these Memoirs, by Kerr.

ly on the cloth, the texture being injured in one part, while in another it was imperfectly whitened. The solution of it in water was therefore substituted.

The acid or bleaching liquor, according to the directions given by Berthollet, is prepared by putting 6 parts of black oxide of manganese and 16 of muriate of soda into a glass, or earthen retort, or a leaden bottle, and pouring upon them 12 parts of sulphuric acid, diluted with 9 of water. The retort or bottle is connected by a tube with a receiver, designed to retain any common muriatic acid that may pass over; from this vessel another tube issues, which is inserted in a large wooden cask filled with water. The tube descends nearly to the bottom of the cask, so that the gas has to rise through the whole body of the water; at the same time, the absorption of it is promoted by the motion of a circular frame within the cask. After the first disengagement of the gas has ceased, heat is applied to the retort, by placing it in a sand bath; or if a leaden bottle be used, by placing it in a vessel of boiling water. So much water is used, that the oxygenated acid is very weak; it requires to be stronger for coarse than for fine cloth, and for linen than for cotton; the average quantity stated by Berthollet is 100 quarts for every pound of muriate of soda that has been used.

The cloth to be bleached is prepared by macerating it in warm water for some hours; it is then boiled in an alkaline ley, prepared from 20 parts of water, and one part of the potash of commerce rendered active by having been mixed with one-third of lime. After boiling it is washed with water, and put into close wooden troughs, containing the oxygenated acid, in which it is allowed to macerate for 3 or 4 hours, pressing the cloth frequently, and renewing its surfaces. It is thus alternately exposed to the action of the alkaline ley and the oxygenated acid, till it is sufficiently bleached, which requires in general from 4 to 8 immersions, according to the nature and coarseness of the

cloth. The subsequent steps of the process are to rub the cloth with soft soap in warm water. This renders the surface more smooth and uniform, and takes away the smell of the oxygenated acid. The cloth is again washed, and is lastly immersed for a short time in water, in which, from a one-sixtieth to a one-hundredth part of sulphuric acid has been dissolved. It thus acquires a finer whiteness, from the sulphuric acid dissolving the remaining colouring matter, as well as a small quantity of iron and calcareous earth contained in all vegetable matter, or deposited in the cloth from the alkaline leys. Lastly, it is exposed to the air for some days, and watered, to carry off any remains of either of the acids, and to remove completely the odour of the oxygenated acid.

Several alterations have been made in the process since it was introduced, and it is now practised in this country in a method different from that above described.

The greatest difficulty attending the use of oxymuriatic acid arose from its suffocating odour, which rendered it almost impossible to work with it in an open vessel, and any apparatus contrived to turn the cloth and expose fresh surfaces of it to the action of the liquid in close vessels, has been found imperfect *.

The addition of an alkali to the liquid removes in a great measure the odour of the acid ; and although it diminishes, to a certain extent, its bleaching power, this is more than compensated for by this advantage. The quantity of alkali which was added amounted to about 1 lb. of the potash or pearlash of commerce to the quantity of acid prepared from 4 lbs. of muriate of soda, the solution of pearlash being deprived of its carbonic acid by the previous addition of lime.

Independent of the weakening of the power of the acid

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* That described by Mr Rupp, Manchester Memoirs, vol. v. is the best, but even it has not been established in use.

by this addition, an expense was introduced by the use of the alkali ; and it became an object of importance to substitute a cheaper substance. Lime was tried, at first in an imperfect manner, but at length with such improvements that it is now always used.

The difficulty of using it arose from the lime being so sparingly dissolved in water, that the solution could have little effect in correcting the odour of the acid. An important improvement, therefore, was that of using lime suspended in water, and kept in suspension by an agitator in a close vessel, into which the gas was transmitted. Its condensation was thus facilitated, and the compound with the lime being soluble in water, the undissolved lime was allowed to subside, and the clear liquor was fit for bleaching. The proportions given by Mr Tennant in the specification of the patent he obtained, were 60 lbs. of lime suspended in 140 gallons of water, or rather, on account of its greater specific gravity, a solution of salt ; this being exposed to the gas from 30 lbs. of oxide of manganese, 30 lbs of sea salt, and 30 lbs. of sulphuric acid previously diluted with its bulk of water.

An improvement of greater importance was made by Mr Tennant of Glasgow, that of combining the oxymuriatic acid with dry lime, and dissolving a certain proportion of this compound in water to form a bleaching liquor. The combination is formed by introducing the oxymuriatic gas through leaden tubes into slaked lime, prepared from chalk, by which it is absorbed. Solutions of this are prepared of different strengths according to the purposes to which they are to be applied, the strength being judged of by the quantity requisite to destroy the colour of a diluted solution of indigo in sulphuric acid.

The process of bleaching, as now performed by these liquors, differs little from that which has been already described as executed by the solution of the oxymuriatic acid alone in water. The practical details with regard to it

will be found in the Art of Bleaching by Pajot des Char-
mes, translated by Nicholson.

Some variations have been introduced for particular pur-
poses.   Mr Ramsay has substituted, with advantage, oxy-
muriate of magnesia for that of lime, in whitening cloth
for calico printing ; the cloth, when lime is used, retaining
a little of it, which in the subsequent operation of clearing
by immersion in weak sulphuric acid, forms sulphate of
lime which remains, and effects the colours when it is
dyed ; while the sulphate of magnesia is so soluble that it
is entirely removed.   Oxymuriate of alumina has been em-
ployed by Mr Wilson to discharge the colour of the Tur-
key-red dye, which resists that of the other oxymuriates,
and is only discharged by oxymuriatic gas, by an opera-
tion very injurious to the workmen.   The preparation of
these substances will be noticed under their history.

The theory of the action of the oxymuriatic acid in
bleaching is simple, as stated by Berthollet.   It depends
merely on the communication of oxygen to the colouring
matter.   It is accordingly found, that the oxymuriatic acid
is converted into muriatic acid : the necessity of water to
this has been already stated.   By this oxygenation of the
colouring matter, the colour is destroyed ; in time, how-
ever, a tint of colour would be regained, and hence, in the
process of bleaching, the advantage of the alternate appli-
cation of an alkaline solution, by which the colouring mat-
ter, rendered more soluble, probably by its oxygenation,
is abstracted.

It has accordingly been discovered, that the alkali itself,
when aided by a high temperature, and the solvent power
of water, is capable of dissolving the colouring matter; and
this either alone, or combined to a certain extent with the
method by the oxymuriatic acid, has been practised with
advantage.   The cloth or thread being impregnated with
a solution of potash or of soda, rendered active by the car-
bonic acid having been abstracted by lime, is suspended

loosely, in a close boiler, a quantity of the same solution being in the bottom, and heat being applied, the boiler having a safety valve in the cover, so that the vapour under pressure may receive a high temperature. It is kept in this situation for a number of hours. The thread or cloth when cold is washed, and either exposed on the field, or subjected to the action of the oxymuriatic acid. It is thus rendered perfectly white. The superiority of this method probably arises from the high temperature, and the solvent power of the watery vapour, favouring the action of the alkali on the colouring matter, while the vapour also penetrates the cloth, so effectually, that that matter is in a great measure dissolved and removed. The application of this method to cleansing linen in hospitals and similar institutions may be regarded too as one of considerable value. On this subject the details given by Chaptal in the memoir quoted beneath, deserve to be consulted *.

Another important application of oxymuriatic acid gas, is that of destroying or neutralizing contagion. Acid vapours, sulphurous acid in particular, under the form of the fumes of burning sulphur, had often been employed for that purpose. Muriatic acid gas had been proposed by Dr J. Johnston, and had been employed by Guyton Morveau on a large scale, in purifying the atmosphere of the cathedral church at Dijon, which had become extremely offensive and noxious from exhalations from cemeteries within the church. Cruickshank afterwards employed oxymuriatic gas, and from the facility with which it decomposes the different compound gases which contain the elements of vegetable and animal matter, and which may be supposed to constitute noxious effluvia, it must probably, where it admits of being applied, be superior to any other agent. It accordingly appears,

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* Nicholson's Journal, 4to, vol. iv, p. 469, vol. v, p. 233. Philosophical Magazine, vol. x, p. 305.

from Guyton's experiments, to correct very speedily any putrid odour *.

THE relations of oxymuriatic acid to the alkalis and earths remain to be stated.

When the gas is transmitted through an alkaline solution sufficiently concentrated, instead of the immediate combination of the oxymuriatic acid and the alkali being established, a quantity of muriate is formed, along with another salt containing muriatic acid and a large portion of oxygen, and which is possessed of very peculiar properties. This is a proof that the oxymuriatic acid has been decomposed. Since a quantity of common muriate is formed, it is evident, as Berthollet, who first observed the fact, concluded, that a portion of it must have parted with its oxygen, to return to the state of muriatic acid; and hence the acid which exists in the other salt that is formed must have a larger proportion of oxygen in its composition than what exists in the oxymuriatic acid. This inference is accordingly established by analysis, the salt formed with the muriate in the above experiment containing a very large quantity of oxygen. This decomposition appears to be owing to the strong attraction of the alkaline base to the muriatic acid, while at the same time the muriatic radical is capable of combining with a larger proportion of oxygen than what exists in the oxymuriatic acid.

From this kind of action, it has been inferred, that no such compounds as those of oxymuriatic acid with the alkalis can be formed, or that no such order of salts as the Oxymuriates exists. This, however, appears to be a mistaken conclusion, and Berthollet shewed that the nature of the combinations which take place when oxymuriatic

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* Guyton, Sur les moyens desinfecter l'Air; or Abstract Nicholson's Journal, vol. xxii.

acid is presented to an alkaline solution, are influenced by the concentration of the solution, so as to produce different results.

If the oxymuriatic gas is condensed by a dilute alkaline solution, or the solution of an alkaline carbonate, the carbonic acid, in the latter case, is disengaged, and a direct combination of the oxymuriatic acid with the alkali appears to be established. The proof of this is, that the liquor has the property of destroying the vegetable colours, and this even in a greater degree than a solution of the oxymuriatic acid in water alone. Now this must be owing to a portion of oxymuriatic acid being present in it, for the salt which contains the large proportion of oxygen, the hyper-oxymuriate, as it is named, has little or no power of this kind; and that it is not owing to a portion of oxymuriatic acid being contained in the liquor in excess, or unsaturated, is proved by this, that the solution has the power of destroying the vegetable colours, even when there is an excess of alkali. Another fact leading to the same conclusion is, that an alkaline solution impregnated with oxymuriatic acid is decomposed by light, and oxygen expelled, and this also where there is a similar excess, so that there can be no free oxymuriatic acid to be decomposed. The proper hyper-oxymuriate suffers no decomposition from light; and the disengagement of oxygen therefore must arise from the decomposition of the portion of oxymuriatic acid in combination with the alkali, and is, of course, a proof of the existence of such a combination.

The same combination can be established with lime even in the solid state, if it is slightly humid, as is apparent from the fact already stated, of this method being employed to condense oxymuriatic acid for the purpose of bleaching. When the compound is submitted to the action of water, a portion of lime is precipitated, and the oxymuriate of

lime remains in solution, possessing the property of destroying vegetable colours.

It is not possible apparently to obtain these compounds pure in a solid or crystallized form, the requisite concentration causing the decomposition of the oxymuriatic acid, and the formation of a muriate and hyper-oxymuriate. They appear to exist neutral, however, in a state of solution, and they display the most characteristic property of salts,—that of decomposing others by double affinity. This is very well shewn in a mode of forming oxymuriate of magnesia, or of alumina, by adding a solution of sulphate of magnesia, or of alumina, to a solution of oxymuriate of lime: the sulphuric acid combines with the lime forming sulphate of lime, which is precipitated, and the oxymuriatic acid remains in combination with the magnesian or aluminous earth.

These oxymuriates are decomposed by heat, as is shewn by submitting the powder of oxymuriate of lime to heat in a tube; oxymuriatic gas is expelled. It is also disengaged by the affusion of an acid, and nearly in the full quantity, as Mr Dalton has shewn, that is estimated by other methods to be present. They slowly suffer spontaneous decomposition; oxymuriate of lime in powder loses considerably when kept of its bleaching power, and muriate of lime is formed. And a solution of potash, impregnated with oxymuriatic gas, was found by Berthollet, after being kept in darkness for fifteen days, not to yield more than half the quantity of oxygen from exposure to light, which a similar portion did when newly formed[*].

The individual oxymuriates will be considered under the history of their respective bases.

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[*] Berthollet, Chemical Statics, vol. ii, p. 146. Dalton, Annals of Philosophy, vol. i. and ii. Wilson, Ibid. vol. viii.

Sect. III.—*Of Per-Oxymuriatic Acid.*

OXYMURIATIC ACID is capable of combining with additional portions of oxygen. It has already been stated, that when it is transmitted through a strong alkaline solution, a solution of potash for example, it suffers decomposition ; a portion of muriate of potash is formed, which remains in solution, and a salt crystallizes in brilliant plates : no oxygen is disengaged during the operation ; it follows, therefore, that the oxymuriatic acid is decomposed, one portion of it yielding oxygen to the other, and each of these becoming saturated by the alkali ; and, accordingly, the salt which crystallizes contains a very large proportion of oxygen, which it yields on exposure to heat. The acid existing in it can be obtained in an insulated form ; and is found also to contain a large proportion of oxygen. Besides this, other two gases have been procured by certain processes from the same salt, each of them containing more oxygen than what exists in oxymuriatic acid.

The precise distinctions of these compounds are not easily determined ; and hence their nomenclature is difficult. The one containing the largest proportion of oxygen has been known, since its discovery, by the name of Hyper-oxymuriatic Acid. Considering it as a compound of oxygen with chlorine as a base, Gay-Lussac has given it the name of Chloric Acid. The one, with the first proportion of oxygen, was named by Davy, Euchlorine Gas; to the other gas which he discovered he gave no name. Gay-Lussac has applied to the intermediate compound between chloric acid and chlorine, the term Chlorous Oxide. It is not certain if the two last are definite com-

pounds; it is perhaps even the more probable opinion
that the Euchlorine gas is a mixture of the other with
Chlorine.   Under this point of view, and in conformity
to the old nomenclature, the intermediate compound be-
tween Oxymuriatic and Hyper-oxymuriatic acids might
be named Per oxymuriatic Acid, and I have accordingly
placed this name at the head of the section under which I
propose to consider these two gases.   If, on the contrary,
they are definite compounds, then considering oxymuria-
tic acid as the base with which the different proportions
of oxygen are combined, the one might be named Prot-
oxymuriatic, and the other Deut-oxymuriatic acid ; and
even considering muriatic acid as the substance with which
these proportions of oxygen are united, these terms might
not be improperly applied, since oxymuriatic acid and
muriatic acid contain, as has already been remarked, the
same proportion of oxygen.   It is evident, however, that
the proper nomenclature can only be established when the
constitution of these compounds is better determined.

The first of them is the Euchlorine Gas of Davy.
When the salt already mentioned, the hyper-oxymuriate
of potash, is acted on by muriatic acid, the latter receives
oxygen from the former, and is converted principally in-
to oxymuriatic acid.   But when a certain proportion of
acid to the salt, and a certain degree of dilution are ob-
served, the euchlorine gas is formed   The hyper-oxy-
muriate, in small crystals, is put into a retort, and twice
as much muriatic acid as will cover it, diluted with an
equal volume of water, is added ; a gentle heat is applied,
and the gas evolved is received over mercury.

The specific gravity of this gas is 2.440.   100 cubic
inches weigh between 74 and 75 grains.   Its colour is
a brilliant yellowish green, more lively than that of chlo-
rine gas, and more inclined to yellow : its smell resembles
that of burnt sugar, mixed with the peculiar smell of oxy-

muriatic gas ; water seems to absorb about eight or ten times its volume of it, and acquires its bright colour. It destroys vegetable colours, but first gives them a tint of red, a fact which proves its acidity.

It sustains combustion, but with less energy than oxymuriatic gas, the metals not inflaming in it, unless heat be applied. Copper, antimony, arsenic, and iron, then burn vividly, the gas being probably decomposed by the heat, and the combustion being supported by the oxymuriatic acid. It does not act on mercury at common temperatures : and therefore, by agitation with that metal, it may be freed from any mixture of oxymuriatic gas. Phosphorus produces a brilliant explosion with it in the cold. Sulphur, introduced inflamed, gives rise to an explosion. Ignited charcoal produces a brilliant flash of light, and then burns with a dull red light. It detonates when kindled with hydrogen, and a great absorption takes place, liquid muriatic acid being formed ; if the hydrogen is in a deficient proportion, a quantity of oxygen is liberated. It yields oxygen to nitric oxide gas, producing red fumes with a diminution of volume. When mixed with muriatic acid gas, a gradual diminution takes place, which is accelerated by heat, oxymuriatic acid is formed, and a dew appears on the vessel.

A striking property of this gas is its exploding from a very slight elevation of temperature ; the heat of the hand is often sufficient to produce the effect ; the explosion is accompanied with the extrication of heat and light, and the gas is resolved into oxymuriatic gas and oxygen, with an enlargement of volume. It is from this circumstance dangerous to operate on large quantities of it. 50 parts of the gas expand to about 60, and when the oxymuriatic gas is removed by water, the remaining oxygen amounts to about 20 parts. It appears, therefore, to consist of 2 parts of oxymuriatic gas and one of oxygen gas by measure ; and the oxygen is condensed in the combination to

half its volume. Converting these into the proportions by weight, they give 81.71 of oxymuriatic acid, and 18.29 of oxygen, or 100 with 22.26.

The other gas stated above to have been discovered by Sir H. Davy, is obtained from the same salt, the hyper-oxymuriate of potash, by the agency of sulphuric acid. When this acid concentrated is poured on the salt, decre-pitations take place, the liquor acquires an orange red co-lour, and a dense yellowish-green vapour floats above. The phenomena of the experiment could scarcely be more minutely examined, for if heat were applied to disengage the vapour, explosion takes place; and if to obviate this the sulphuric acid is previously diluted, oxymuriatic acid gas principally is disengaged. Sir H. Davy, however, em-ployed the following method. The dry hyper-oxymuriate in powder is mixed with a small quantity of sulphuric acid, and they are rubbed together with a spatula of platina un-til they have incorporated and formed a solid mass of an orange colour. This is introduced into a small glass re-tort, and exposed to the heat of water gradually warmed: a gas is disengaged of a bright yellowish-green colour, which is rapidly absorbed by water, but has no sensible ac-tion on mercury. That the experiment may be without danger, not more than fifty grains of the hyper-oxymuriate should be employed: great care should be taken to prevent any combustible matter being present, and the water should not be allowed to attain a temperature so high as 212°. Nitric acid affords the same gas, and with less risk, but mixed with a portion of oxygen.

This gas has a much more brilliant colour than euchlo-rine gas, is more rapidly absorbed by water, has a peculiar and more aromatic smell, unmixed with any smell of chlo-rine. It destroys moist vegetable blues without reddening them. When it is heated to a temperature above that of 212°, it explodes with more violence than euchlorine, and

greater enlargement of volume, producing much light. None of the combustible bodies decompose it at common temperatures except phosphorus ; it, when introduced, occasions an explosion, and burns in the chlorine and oxygen gases, which are liberated with great brilliancy.

The saturated solution of the gas in water is of a deep yellow colour ; its taste is not sour, but astringent and acrid. It exhales white vapours : exposed to the air, or even kept in close vessels, it soon becomes colourless, a change probably owing to decomposition. When added to a solution of any of the alkalis, it does not immediately lose its colour, nor produce neutralization ; but after some time the effect is produced, and a hyper-oxymuriate (probably with a portion of muriate) is formed.

The gas in its explosion by heat is resolved into oxygen and oxymuriatic gases ; the expansion is equal to three volumes, from two of the gas ; and of these three volumes two are oxygen gas, and one oxymuriatic gas. Converting these into weight, the proportions are 53 of the latter and 47 of the former, or 100 with 89 *.

Von Stadion has given a similar process by which a compound analogous to this is obtained. Hyper-oxymuriate of potash is fused in a retort, and when cold concentrated sulphuric acid is poured over it, the mixture is exposed for three hours to the heat of a water-bath gradually raised from 55° to 212° ; a gas comes over, which is to be received over mercury. It is of a lively yellow colour, more intense than that of euchlorine ; its smell is peculiar ; it does not alter blue paper ; it remains unaltered in the dark, but when exposed to the rays of the sun its volume is enlarged, and it is resolved into chlorine and oxygen. The agency of heat, and of the electric spark, produces the same decomposition ; at a temperature between 144 and 212° it explodes. When mixed with hydrogen gas,

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* Philosophical Transactions, 1815.

and detonated by the electric spark, it is resolved into muriatic acid and water, requiring 8 measures of hydrogen to 3 measures for its entire decomposition. Water absorbs seven times the volume of the gas. The solution has a deep yellow colour, a pungent taste, and peculiar odour. It remains in the dark without any change, but when exposed to the solar rays is resolved into chlorine, and the hyper-oxymuriatic acid or chloric acid of Gay-Lussac: the former may be expelled by heat, and the latter remains pure. The composition of this gas may be inferred from its decomposition by the electric spark over mercury ; the chlorine into which it is resolved is absorbed by the quicksilver, and the residual oxygen is equal to the original volume : the volume of the chlorine after the decomposition is inferred from other results to have been to that of the oxygen as two to three ; hence the proportions are represented by two volumes of chlorine and three of oxygen *.

It is evident that a degree of obscurity remains with regard to these combinations. The two last, though similar, are not altogether the same in properties, and they differ in the proportions in their composition. The euchlorine is altogether different from either ; the question remains whether it is to be considered as a definite compound or not. The small quantity of oxygen it contains compared with that in the others, and which it is scarcely possible to reconcile by any series of multiples according to the usual laws of definite combinations, renders this doubtful. It is not improbable, therefore, that it is a mixture or compound containing oxymuriatic acid. Sir H. Davy remarked, that two volumes of the gas which he had last discovered, and three of chlorine, would give by detonation precisely the same products as euchlorine, and the latter, he added, may be of this composition. The whole subject must remain for farther experimental investigation.

* Annals of Philosophy, vol. ix, p. 22.

Sect. IV.—*Of Hyper-oxymuriatic Acid.*

THE acid to which this name has been applied is form-
ed when oxymuriatic gas is transmitted through an alka-
line solution of a certain degree of strength. Four parts
of subcarbonate of potash are dissolved in 16 of water, and
two parts of lime are added to abstract the carbonic acid.
The solution being filtered, is put into the bottles of
Woolfe's apparatus, connected with a retort containing a
mixture of muriate of soda, black oxide of manganese, and
sulphuric acid in the proportions affording oxymuriatic
acid: the first bottle contains a little water to condense
what common muriatic acid gas passes over. The trans-
mission of the oxymuriatic gas is continued, until the li-
quor appears to contain it in slight excess; a salt is depo-
sited by spontaneous crystallization in scales, which, when
removed and washed with a small quantity of water, is
white and brilliant. A portion of muriate of potash is at
the same time formed, and remains in solution. It fol-
lows from this, as has been already remarked, that the
oxymuriatic acid suffers decomposition from the action of
the salifiable base; one portion of it yields oxygen to the
other; one returns to the state of muriatic; the other pass-
es to the state of hyper-oxymuriatic acid, and each of these
becomes saturated with the alkali, so as to form the two
salts. This conclusion equally follows from the nature of
the crystallized salt; it contains a large proportion of oxy-
gen, which may be expelled from it at a red heat, and mu-
riate of potash remains. According to the other doctrine,
it must be supposed, that from the action of the chlorine
and the salifiable base, water is decomposed; its hydrogen,
with a portion of the former, forms muriatic acid, and its
oxygen, with another portion of it, enters into the constitu-
tion of the salt.

Though the existence of this acid had been inferred by

Berthollet at an early period from these results, it had not been procured in an insulated form, until a process by which this is effected was given by Gay-Lussac. Chenevix had given a method of preparing hyper-oxymuriate of barytes, that of transmitting oxymuriatic acid gas through water, in which pure barytic earth is diffused; hyper-oxymuriate and muriate of barytes are formed, and as they are nearly of the same degree of solubility, the filtered liquor is to be boiled with phosphate of silver ; this decomposes the muriate of barytes, forming phosphate of barytes and muriate of silver, which being both insoluble, the hyper-oxymuriate of barytes remains in solution, and by evaporation may be obtained crystallized. Gay-Lussac's process is to drop into a dilute solution of this salt, very weak sulphuric acid; sulphate of barytes is immediately precipitated, and by continuing the addition, taking care to avoid any excess, the pure hyper-oxymuriatic acid remains in solution. That it suffers no decomposition in being thus disengaged, is proved by there being no escape of oxygen, and no production of muriatic acid, the liquor suffering no precipitation from nitrate of silver *. Gay-Lussac, considering this acid as composed of chlorine as a base combined with oxygen, has given it the name of Chloric acid, and its salts he names Chlorates. The following are its properties.

It is colourless ; has no sensible smell ; according to

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* Annales de Chimie, tom. xcvi.

Vauquelin has given some additional directions for conducting this process, (Annales de Chimie, t. 93, 95.) The action of the phosphate of silver on the hyper-oxymuriate is, from its insolubility, very slow. To obviate this, Chenevix added a little acetic acid, which dissolves the phosphate. Vauquelin found, however, that a little acetate of barytes is thus formed, which adheres to the hyper-oxymuriate of barytes; and in one experiment in which the salt had been exposed to heat, the presence of this gave rise to a very violent detonation,

Vauquelin, however, when concentrated, and it is a little warm, its odour is somewhat pungent; its taste is acid and astringent. It reddens litmus, and does not immediately destroy the colour; but after a few days the colour is lost; or if litmus paper be dipt in the acid and exposed to the air, as it becomes concentrated by evaporation, the colour is weakened, and the paper at length becomes white; it does not cause any alteration in the more permanent colour of the solution of indigo in sulphuric acid. Light does not decompose it. By a gentle heat it may be concentrated without evaporation or decomposition; when concentrated it acquires somewhat of an oily consistence; it suffers no loss from exposure to the air. When submitted to a higher heat it is partly volatilized, and partly decomposed, being resolved into oxygen and chlorine. Muriatic, sulphuric and sulphurous acids produce a similar decomposition, the muriatic and sulphurous acids attracting the oxygen and liberating the chlorine: nitric acid causes no change. It combines with the alkalis, and forms salts, perfectly similar to the hyper-oxymuriates. It does not precipitate nitrate of silver, of mercury, or of lead, nor indeed any other metallic solution.

The constitution of this acid seems to be preserved by its combination with water; and hence it cannot pass into the gaseous state without decomposition. In this respect it is similar to the other acids, to which water is necessary in the insulated form. Gay-Lussac infers that it is composed of 1 volume of chlorine with 2.5 of oxygen, or by weight 100 with 113.95. From the quantity of oxygen given out by the hyper-oxymuriate of potash, and the proportion of muriatic acid in the muriate of potash which remains, the proportions are 100 of chlorine with 111.68 of oxygen. These estimates refer, however, to the real acid as it is called, or acid free from water. As it cannot exist apart from a salifiable base without this water, that is, without the elements of water in a certain proportion,

it is to be regarded as a ternary compound, containing both oxygen and hydrogen combined with its radical. The proportions in this acid do not lessen the difficulty which exists with regard to the series of combinations in the others. Considering euchlorine as the first compound, the proportion of oxygen to chlorine in its composition is to that of the second compound, as 1 to 4, and to the third or chloric acid as 1 to 5, and no series can be traced to connect these by any regular progression.

Hyper-oxymuriatic acid or chloric acid combines with the different salifiable bases. Its salts, named Hyper-oxymuriates or Chlorates, are distinguished by affording pure oxygen gas when exposed to a red heat, detonating with great violence with inflammable bodies, either on the application of heat or by percussion or trituration, and causing such bodies to burn when sulphuric or nitric acid is added to the mixture of the salt and the inflammable matter. They decrepitate on mere trituration. Their taste is cool and penetrating ; they are generally soluble in water, and crystallizable ; the greater number of them are also soluble in alkohol. They do not precipitate any of the metallic salts. They do not destroy the vegetable colours ; but rather in small quantity heighten their brilliancy. These compounds individually will be noticed under their respective bases.

Von Stadion has described what he considers as an oxychloric acid. After the first and more violent action of sulphuric acid on hyper-oxymuriate of potash has ceased, if heat is applied until the yellow colour of the mass disappears, the residue consists of a salt containing this acid, mixed with supersulphate of potash. They may be separated by crystallization, and if to the former salt an equal weight of sulphuric acid be added, and a heat of 280° be applied, the acid it contains may be distilled over. It consists, he infers, of 2.56 of chlorine, and 4 of oxygen,

and in relation, therefore, to the other compounds, contains the latter element in the proportion of 7. Its analysis does not appear, however, to have been executed with much precision, being inferred only from the composition of the salt, and scarcely any specific properties are ascribed to it *.

In concluding the history of the combinations of muriatic acid with oxygen, it remains to take notice of a compound acid, having some relation to the oxymuriatic, formed by the mixture of muriatic and nitric acids. It was known to the older chemists by the name of Aqua Regia, from being the solvent of gold, and has since been denominated from its composition NITRO-MURIATIC ACID.

When the two acids are mixed together, in the proportion of one part of muriatic to two of nitric, the temperature rises, the mixed fluid acquires a deep orange or red colour; the smell of oxymuriatic acid becomes strong, and at length an effervescence from the disengagement of an elastic fluid takes place. A similar compound is formed by adding a muriate, such as muriate of ammonia, to nitric acid. The gas disengaged during the mutual action is nitric oxide gas, mixed with oxymuriatic gas, a proof that the nitric acid is decomposed, and a part of its oxygen tranferred to the muriatic acid, forming the oxymuriatic acid disengaged; the compound acid thus formed consists of muriatic acid, probably of a portion of oxymuriatic acid, and of undecomposed nitric acid surcharged with nitric oxide. The formation of the oxymuriatic acid is not owing simply to the superior affinity of muriatic acid to oxygen, but in part to the affinity of nitric acid to nitric oxide, or nitrous acid. Hence, as soon as nitric oxide is formed in as large

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* Annals of Philosophy, vol. ix, p. 23.

quantity as the liquid can hold dissolved, the farther de-
composition ceases, though there may be a portion of ni-
tric acid still undecomposed, and although a fresh quan-
tity of muriatic acid be added. And muriatic acid, added
to fuming nitrous acid, does not produce much sensible
change.

Nitro-muriatic acid, then, appears to consist of nitric and
muriatic acids, with nitric oxide, and probably oxymuria-
tic acid.   Whether these constituent ingredients are in
combination or not is not apparent.   When an alkali is
added to saturation it combines with the nitric and muria-
tic acids, forming the two separate salts, and the nitric ox-
ide is disengaged.

The peculiar action of this acid on the metals has been
ascribed to the oxymuriatic acid believed to exist in it;
but, according to Berthollet, it depends on the facility of
decomposition of the nitric acid, aided by the affinity of the
muriatic acid to the metallic oxide,—the metal receives
oxygen from the nitric, and the oxide combines with the
muriatic acid ; the affinity of the latter promoting the de-
composition of the former, and consequently the oxidation
and solution of the metal.   Hence the action is more en-
ergetic than that of liquid oxymuriatic acid.   The com-
pound acid is principally used in some operations on the
metals, particularly in assaying.

CHAP. VII.

OF FLUORIC ACID.

For the discovery of this acid we are indebted to Scheele. It exists in the fossil known by the name of Fluor Spar, combined with lime ; it was from this native combination that Scheele obtained it, and by a series of admirable experiments, demonstrated that it is a peculiar acid different from all others. Scheele did not obtain it, however, in a pure state, nor was it known in this state previous to the researches a few years ago of Gay-Lussac and Thenard, and their discoveries with regard to it were highly important both from the facts and the views they introduced.

Though the compound of fluoric acid with lime exists in considerable quantity in nature, the acid had scarcely, until lately, been known to exist in any other fossil. Klaproth discovered it in the Saxon topaz. This was confirmed by Vauquelin, who has found it also in the Brazilian topaz. It is the principal ingredient in the Cryolite, a fossil found in Greenland. It has also been discovered in the animal kindgom. Morichini, an Italian Chemist, in analysing the enamel of the fossil or petrified teeth of the elephant, found it to be principally a combination of fluoric acid and lime. He afterwards detected it in the enamel of the human teeth. Gay-Lussac, prosecuting these researches, found it to exist in ivory [*]. And Berzelius has found fluate of lime, both in the enamel, and in the osseous part of the teeth [†].

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[*] Philosophical Magazine, vol. xxiii, p. 264.
[†] Nicholson's Journal, vol. xviii, p. 75.

To obtain fluoric acid, the process usually followed is to add one part of sulphuric acid to an equal weight of fluor spar, coarsely pounded, in a lead bason, or matrass; the sulphuric acid combines with the lime of the fluor spar, and the fluoric acid is disengaged in the form of gas. The gas is collected over mercury, as it is quickly absorbed by water. There is much difficulty, however, in subjecting it to experiment, from a singular property belonging to it, that of acting rapidly on siliceous earth, and dissolving it. Hence, as glass is composed of this earth, it is speedily corroded,—and glass vessels cannot be used to confine it, without altering its purity, by contaminating it with siliceous earth. It now appears, from the researches of Gay-Lussac and Thenard, that the acid had not been obtained free from this earth, the fluor spar generally containing a portion of it; or glass vessels being so rapidly acted on that the acid disengaged from a pure fluor is immediately contaminated with silica; and this has an effect on its properties so important, that those of the pure acid are totally different from what was formerly supposed. For an account of them we are entirely indebted to these chemists[*].

The process they employed to obtain it is to select fluor spar, pure, and in particular free from silica. It is reduced to powder, and mixed with twice its weight of concentrated sulphuric acid in a leaden retort, to which is adapted and secured by lute, a wide leaden tube curved towards the middle, and having at its other extremity a very small aperture. Heat is applied gradually to the retort, and the leaden tube or receiver is kept cool with ice. An ebullition is soon heard, which is owing to the disengagement of the fluoric acid : it does not exist as a permanent gas, as had hitherto been believed, but condenses in the liquid form.

This liquid acid retains its fluidity at 60° of Fahrenheit,

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[*] Recherches Physico-Chimiques, tom. ii, p. 1.

and also at zero, and even a number of degrees below it, not congealing at —4° of Fahrenheit; it boils at a heat which is not very high. To retain it in the liquid form, it is necessary to preserve it from the contact of the air, otherwise it evaporates speedily: it must be preserved in metallic vessels, as all others are acted on : those of lead answer, but silver, from its greater hardness, so that vessels of it can be better closed, is preferable. When the acid comes in contact with the air, it immediately diffuses dense vapours, by combining with the humidity of the atmosphere. Its odour is extremely penetrating, and its vapour dangerous to inspire. When dropt into water considerable heat is produced, so that each drop in combining with the water makes a noise similar to that from the immersion of red hot iron ; the heat therefore is much above that from sulphuric acid ; if a few drops of water are added to the acid, it brings it suddenly into ebullition.

As soon as the liquid acid is brought into contact with glass it obscures it, becomes much heated, evaporates, and passes into a permanent gas, the same as that which had before been considered as a fluoric acid ; this is owing to its dissolving a portion of the silica of the glass : it quickly saturates itself with this earth, and a small quantity is sufficient to produce this change. If the liquid acid be diluted with water, it still acts on glass, but does not pass into the gaseous form.

Of all the properties of this acid, the most extraordinary is its action on the skin; it destroys it the moment it touches it, a severe pain is felt, the surrounding parts become white and painful, and a vesicle is formed, which is soon filled with purulent matter. The smallest quantity of the acid produces these effects, though more slowly, and they are attended with irritation of the general system ; it is therefore necessary to observe the utmost precaution in experiments with it ; Gay-Lussac and Thenard, notwithstanding all their care, were repeatedly injured by

it. If any part of the lute give way during its prepara-
tion, no attempt must be made to repair it ; and even in
pouring it from the receiver, care must be taken that no
drop has run down the side.

Gay-Lusssac and Thenard examined the combinations
of this acid with salifiable bases. Those with the alkalis
are sapid and soluble in water. Those with the earths
are in general insoluble, but are rendered soluble by an
excess of acid. A very singular result is stated by these
chemists, as occurring in the formation of some of these
earthy fluates by double decomposition. If fluate of po-
tash, for example, and muriate of glucine, both neutral,
or even with an excess of acid be mixed together, the li-
quor from their mixture is alkaline, without the precipi-
tate of fluate of glucine, which subsides, having become
acid. The same phenomenon is exhibited in the forma-
tion of the fluates of zircon and ittria ; they are precipitated
when formed by mixing fluate of potash and the muriates
of these earths ; and even when these salts are sensibly
acid the liquor remains alkaline, while the earthy fluate
which is precipitated is not sensibly acid. It is the only
exception which has been observed to the law which has
been stated, (p. 176.), that the powers of neutralization in
acids and in the bases with which they combine, are such,
that when new combinations are formed by the mixture of
two neutral salts, the state of neutralization is preserved.
The individual fluates are to be afterwards considered.

The relation of fluoric acid to siliceous earth has been in
part stated in the previous account of it. The peculiar
property of this earth is that of being little, if at all acted
on in the humid way by any acid except the fluoric, and
the power of acting on this earth is not less characteristic
of this acid. The combination is effected with great fa-
cility, and in different proportions. When fluoric acid
is disengaged from fluate of lime by any other acid, if the
experiment be made in a glass-vessel, part of the silica of

the glass is always dissolved ; or if a little flint in powder has been mixed with the materials, the acid gas holds dissolved a large portion of silica. It retains it in solution, when received over quicksilver ; but when presented to water, a considerable part of the silica is separated, and forms a gelatinous matter, retaining a little acid, and the acid absorbed by the water retains a little of the earth. If the pure liquid acid be put into a glass-vessel, it instantly dissolves silica and becomes gaseous ; the acid in its common state acts on glass slowly.

The liquid fluoric acid does not act with much energy on the metals. When diluted with seven parts of water, it dissolves zinc, the solution being attended with a disengagement of hydrogen gas ; when less diluted it dissolves iron but slowly ; it does not dissolve tin, copper, quicksilver, lead, nor indeed the greater number of the metals : but it combines with their oxides, forming compounds which are in general insoluble, and frequently gelatinous.

It remains to state the properties of the SILICEO-FLUORIC ACID, as it may be named, the substance formerly regarded by chemists as fluoric acid. Gay Lussac and Thenard and J. Davy have added some facts with regard to what was before known of it *.

The process usually followed to obtain it, was that of decomposing fluor spar by sulphuric acid, with the application of a moderate heat : but the fluor spar containing in general a little siliceous earth, or a glass retort being employed in the preparation, the acid was evolved in combination with silica. To obtain it with certainty saturated, and at the same time to prevent the erosion of the retort, a little pounded flint or pounded glass may be mixed with the fluor spar, previous to the affusion of the sulphu-

* Recherches Physico-Chimiques. Philosophical Transactions, 1812.

ric acid; on applying a moderate heat the silicco-fluoric
acid gas is disengaged.

Siliceo-fluoric acid exists as a permanent gas ; it is one
of the heaviest of the gases ; its specific gravity, according
to the estimate of J. Davy, being 3.57.   100 cubic inches
weigh 110.78 grains.   It has a pungent irritating odour ;
is corrosive; extinguishes combustion, and exhibits un-
equivocal acid powers.   It forms white vapours when pre-
sented to the atmosphere by combining with its humidity,
and is immediately absorbed by water in large quantity,
equal, according to Mr J. Davy, to 365 times its volume.
In this absorption, however, it undergoes decomposition,
a portion of siliceous matter is precipitated, and a super-
fluate, or, as it has been named, Sub-Siliceo Fluoric Acid,
remains in solution.   The liquid is very acid, corrosive,
and acts on glass.

To determine the proportion of silica in the composition
of this gas, Mr J. Davy neutralized it, by receiving it in
liquid ammonia ; the whole of the earth was precipitated,
and from the quantity of it he inferred the proportions to
be 61.4 of silica and 38.6 of fluoric acid.   The sub-siliceo-
fluoric acid formed by the decomposition of the gas by wa-
ter, consists, independent of the presence of water, of 54.56
of silica and 45.44 of acid.   This liquid acid evaporates
when exposed to the air, leaving scarcely any residue; when
gently heated it is dissipated in white fumes.   Muriatic acid
gas and concentrated sulphuric acid expel from it siliceo-
fluoric acid gas.

The siliceo-fluoric acid, either gaseous or combined with
water, acts with little energy on inflammables or on the
metals.   Those which decompose water, as zinc or iron, it
dissolves slowly, with an evolution of hydrogen.

It combines with the alkalis and earths, suffering at the
same time partial decomposition. These compounds, which
were formerly considered as fluates, appear to be ternary
compounds, the acid always retaining a portion of silica in

solution. They will fall to be noticed individually with their respective bases.

The composition of fluoric acid, it has been stated, was unknown to chemists. After the discovery of potassium, its powerful chemical agency was employed with the view of decomposing it. The results are different, as the siliceo-fluoric, or the pure fluoric acid is operated on.

Gay Lussac and Thenard, in submitting potassium to the action of siliceo-fluoric acid gas, found, that when melted by a moderate heat it burns vividly, the gas is absorbed, there is little disengagement of hydrogen, the potassium disappears, and is replaced by a solid substance of a reddish-brown colour. On submitting this to the action of water, hydrogen was slowly disengaged, in quantity inferior to that which the potassium would have produced, and the water was found to hold in solution fluate of potash with an excess of alkali. A substance remained undissolved of a reddish-brown colour; when heated it burns, oxygen is consumed, siliceo fluoric acid gas is produced, and a part becomes soluble, which appears to be fluate of potash : the insoluble part is fluate of potash and silica. In these experiments, they considered it probable that the fluoric acid had been decomposed, and its base combined with the alkali formed by the oxygenation of the potassium, forming a fluuret analogous in constitution to an alkaline phosphuret, which has the power of decomposing water [*]. The same results nearly were obtained by Davy, in performing similar experiments [†].

Gay-Lussac and Thenard, after their discovery of pure fluoric acid, submitted it to the action of potassium. On introducing a small quantity into the liquid acid in a copper tube, a loud detonation took place, with heat and light, and an abundant extrication of dense vapours. To

[*] Nicholson's Journal, vol. xxiv, p. 29. Recherches, tom. ii.
[†] Philosophical Transactions, 1809.

moderate this violent action, the acid was brought to act
slowly on the potassium, and without the access of air;
combustion was thus avoided, though considerable heat was
produced, with the disengagement of gas which they found
to be hydrogen ; a solution of acidulous fluate of potash
remained in the tube.   These results, therefore, had been
owing to the agency of water, its oxygen being attracted
by the potassium, and the potash formed combining with
the acid. Thus the fluoric acid contains, like other power-
ful acids, combined water *.

They endeavoured to procure it free from water, but
without success, though combinations of it were procured
in which they inferred it to be in that state.   In decom-
posing fluor spar by dry boracic acid, they obtained a gas
composed of fluoric and boracic acids, fluo-boric acid as
they named it, which did not appear to contain combined
water.   On heating potassium in this gas it burned vivid-
ly, the whole gas was condensed when the due propor-
tions were observed, and the potassium was converted into
a solid, having no longer metallic lustre, and of a choco-
late colour, having little taste, and fusible at a red heat.
Brought into contact with water, a few bubbles of hydro-
gen are extricated, and it is in a great measure dissolved.
The part dissolved is fluate of potash ; the undissolved part
remained in the form of flocculi, of a deep chocolate co-
lour, and was found to be boron, the base of boracic acid.

In the siliceo-fluoric acid gas, water does not appear to
be present, as little hydrogen is evolved in the combustion
of potassium in it.   They therefore repeated this experi-
ment to ascertain the product : they obtained the same
brown coloured substance which they had before observed,
and found reason to conclude as before, that it consists of
a portion of superfluate of potash and silica, with the pe-
culiar inflammable matter which they consider as contain-

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* Mémoires d'Arcueil, tom. ii, p. 325.

ing the base of the acid, probably in combination with po-
tash. But they could not succeed in obtaining it in an
insulated form *.

It appears, therefore, from these researches, that fluoric
acid, like sulphuric, nitric, and muriatic acids, contains a
portion of combined water, from which it cannot be ob-
tained separate ; and like muriatic acid it parts with this
water when it enters into combination, not only with sa-
lifiable bases which neutralize it, but with others in which
it retains its acidity to a certain extent. In oxymuriatic
acid, muriatic acid exists without combined water; and in
fluo-boric acid, and siliceo-fluoric acid, fluoric acid exists
in like manner free from water. It appears, too, that fluo-
ric acid like muriatic acid cannot be disengaged from its
combinations, without this portion of water being supplied.
In disengaging it from fluate of lime by sulphuric acid,
this acid affords this water. But when the French che-
mists attempted to disengage it from fluate of lime by the
vitreous super-phosphate of lime, though a very strong
heat was applied there was no sensible decomposition. All
these facts confirm the general analogy with regard to the
other powerful acids.

It was very obvious, after the theory of chlorine had
been proposed, that a similar view might be applied to
explain these facts,—that fluoric acid, not capable of be-
ing resolved into any acidifiable base, might be held to be
composed of hydrogen, with a principle analogous to chlo-
rine. This was accordingly suggested by M. Ampere.
He supposed the existence of such a principle, which he
called Fluorine; combined with hydrogen, it forms fluoric
acid ; with silicon, siliceo-fluoric acid; with boron, fluo-
boric acid ; with the metallic base of lime, fluor spar ; and
with other metals, the different dry fluates. This opinion
was adopted by Sir H. Davy, and he endeavoured, in a

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* Recherches Physico-Chimiques, tom. ii, p. 61.

number of experiments, to obtain this principle, or gain distinct evidence of its existence *. But all these attempts failed, nor have any subsequent investigations been more successful, though those who support the theory of chlorine have generally also (forgetting strictness of induction) maintained the existence of fluorine. It is, however, entirely hypothetical; and even if it were obtained, it would, from the weight of analogy, be regarded with most probability as Oxy-fluoric acid, the binary compound of an acidifiable radical, fluoron, with oxygen. And admitting the view I have illustrated, Fluoric acid would be a compound of the same radical with oxygen and hydrogen; Siliceo-fluoric acid, a ternary compound of fluoron, silicon and oxygen; and Fluo-boric acid, a ternary compound of fluoron, boron, and oxygen.

Of the applications of Fluoric acid, the only one of any importance is that for etching or engraving on glass, depending on its agency of dissolving siliceous earth. The glass is covered with a thin coat of wax, or is brushed over with a solution of isinglass in water; and when this is dried, lines are easily traced by a graver. It is then exposed to the action of the acid in the state of gas; the parts of the glass thus exposed are soon eroded; the impression being more or less deep, according to the time during which it is exposed. Such a method, were it possible to obviate completely the defect from the brittleness of glass, has, from the hardness of that substance, the important advantage over copper, that the impressions do not become less delicate from the fineness of the lines being diminished by the pressure in throwing them off. Different methods have been proposed to render the method practicable †, and engravings, though not of much delica-

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* Philosophical Transactions, 1813, 1814.

† { Nicholson's Journal, 4to, vol. ii, p. 60.
Philosophical Magazine, vol. xvii, p. 357.
Journal de Physique, tom. xxxii, p. 419.

cy, have even been taken. In this application the pure
liquid fluoric acid, diluted with water, Gay-Lussac and
Thenard have observed, must be preferable to the acid
under the form in which it has been hitherto used.

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The name of FLUO-BORIC ACID was given by Gay-
Lussac and Thenard to a compound of fluoric and bora-
cid acids which they discovered, and which is possessed of
very singular and important properties. Its history is taken
from their memoir *.

It was obtained, I have already stated, in an experiment
designed to obtain fluoric acid if possible without water,
that of expelling it from fluate of lime by dry boracic acid.
A mixture of 2 parts of pure fluate of lime, with one part
of vitrified boracic acid, was introduced into a coated iron
tube, to which a glass tube was adapted, terminating un-
der an inverted jar filled with quicksilver. On applying a
red heat, dense vapours were disengaged from the produc-
tion of fluo-boric acid gas. Dr J. Davy gave an easier
process to obtain it, mixing two parts of fluor spar, one
part of dry vitreous boracic acid and twelve parts of sul-
phuric acid in a retort, and applying a moderate heat; the
fluo-boric acid gas is formed, and disengaged, and may be
received over mercury †.

This gas has a specific gravity of 2.371: 100 cubic inches
of it weigh 73.5 grains; it is without colour; its odour is
penetrating, and resembling that of siliceo-fluoric gas; it
extinguishes combustion, and reddens powerfully the ve-
getable colours. When presented to air containing hy-
grometric water, vapours are formed as dense as those
which are produced by the mixture of muriatic acid and
ammoniacal gases: if the air is dry this appearance does
not take place, and it is greater as the air is more humid.

* Recherches Physico Chimiques. t. ii, p. 37.
† Philosophical Transactions, 1812.

The gas exerts no action on glass. It acts powerfully on animal and vegetable substances ; in this respect its action is as energetic as that of sulphuric acid, and appears to be of a similar nature, that of causing a formation of water and evolution of charcoal. It thus converts alkohol into an ether, and blackens the driest paper, forming at the same time vapours from the production of water. It does not exert the violent action of fluoric acid on the skin.

Fluo-boric acid gas is absorbed by water, in very large quantity, and with the utmost rapidity : if there is any insoluble gas mingled with it, this impedes the rapidity of absorption. It requires the transmission of the gas through a small quantity of water for a long time before the water is saturated with it, much heat is produced, and there is an enlargement of volume. The water, when saturated at 50, has absorbed 700 times its volume, and is of the specific gravity 1.77. The solution is limpid, extremely caustic, and exhales abundant vapours. Not more than a fiftieth part of what the solution contains can be expelled by heat. It then resembles sulphuric acid in appearance and causticity ; like it too it does not boil but at a temperature much superior to that of boiling water, and it condenses in streaks, forming a liquid which contains a very large portion of the gas.

This acid combines easily with the different salifiable bases. It was by saturating its solution with ammonia, and decomposing the salt formed, that Gay-Lussac and Thenard discovered its nature. Having evaporated the liquor to dryness, they exposed the solid matter to a red heat; they obtained a residue which calcined in a crucible, melted, and was found to be boracic acid. The salt which sublimed was fluate of ammonia, with a portion of borate of ammonia. These results, they inferred, proved the salt to be a triple one, consisting of the fluoric and boracic acids in combination with soda, and thus pointed out the constitution of the fluo-boric acid. It is probable, they add, that

there exist analogous compounds with the different bases, —ternary compounds of fluoric and boracic acids with the alkalis and earths.

Potassium when heated in the gas inflames ; and a substance is formed, which, after having been submitted to water, gives a residue which is principally a boron with fluate of potash, which is dissolved by the water. The other views that have been since given of the constitution of this acid have been stated above.

Fluo-boric acid gas, from its strong attraction to water, and the dense vapours which it forms on combining with it in the elastic form, is the most powerful of all reagents in detecting the presence of hygrometric water in gases. The application of it by Gay-Lussac and Thenard with this view, and the results, have been already stated under the history of water.

CHAP. VIII.

OF IODINE, HYDRIODIC AND OXIODIC ACIDS.

THE name IODE or IODINE has been given to a singu-
lar substance, discovered within these few years, and ex-
tremely interesting from being more analogous in its che-
mical relations than any other body to Chlorine. The dis-
covery of it is due to Courtois, a chemical manufacturer at
Paris. He conducted a manufactory of soda from barilla
or kelp; and he remarked, that the iron vessels employ-
ed in the calcinations and evaporations in his process, were
more corroded than there appeared any adequate cause
for. In investigating this, he obtained a quantity of this
substance, no trace of which had been before observed.
He gave it to Clement, who made some experiments upon
it, the results of which were communicated to the French
Institute. Gay-Lussac, too, immediately undertook an
investigation of it; and it attracted the attention of Vau-
quelin, Sir H. Davy, and other chemists *. It forms with
hydrogen a peculiar acid, which has been named Hydrio-
dic Acid. It also unites with oxygen, forming another
acid, which has been denominated iodic, but which, for
more accurate distinction, may be named Oxiodic Acid.
Gay Lussac, at a period subsequent to his first investiga-
tion, published an elaborate memoir on the properties and
combinations of these bodies †, from which, and from Sir

* Annales de Chimie, tom. lxxxviii. xc.
† Ibid. tom. xci.

H. Davy's memoirs *, principally the following account of them is taken.

It may be proper to make the preliminary observation, that Iodine and the acids it forms may be considered under the same point of view as Chlorine, and muriatic and hyper-muriatic acids. It may be looked upon as a simple substance, which by direct combination with hydrogen and with oxygen forms the two acids. Or it is possible that it may be a compound of a radical with oxygen; oxiodic acid may be a similar compound with a larger proportion of oxygen; and hydriodic acid, another compound with combined water, or with the elements of water. The first of these is the theory which follows by most direct inference from the facts at present known. But either of the others is a possible view, and is better supported perhaps by weight of analogy. It is at least necessary to keep these under notice in considering its chemical relations.

Sect. I.—*Of Iodine.*

Iodine is always procured from kelp or barilla. It appears to exist in these in the state of a saline compound, probably in the state of hydriodic acid combined with soda. To obtain the iodine from this with more facility, and in a pure state, it is necessary to remove as much as possible the sulphur which is present in the state of sulphuret of soda, and the muriatic acid in that of muriate of soda. The kelp or barilla, therefore, is lixiviated repeatedly with water, so as to yield all its soluble matter; the solution is boiled down; the muriate of soda which is

* Philosophical Transactions, 1814, 1815.

separated during the evaporation is removed; the liquor
when sufficiently concentrated is allowed to remain expos-
ed, until the carbonate of soda is abstracted as far as pos-
sible by crystallization.   To the residual liquor, diluted
if necessary, sulphuric acid is dropt in, in successive por-
tions, as long as any precipitation of sulphur, or disen-
gagement of sulphuretted hydrogen, or muriatic acid gas
takes place.   It is then evaporated till a dry saline mass is
obtained.   This affords the iodine.   Different methods may
be employed to afford it.   If the salt is put into a tube
or retort, and half its weight of sulphuric acid be poured
upon it, a purple-coloured vapour arises, which is the io-
dine; and on applying a moderate heat it becomes more
abundant, and condenses in crystalline scales or needles,
in the neck of the retort or upper part of the tube.   If to
the salt having in it a slight excess of acid, about a sixth
of its weight of black oxide of manganese be added, on ap-
plying heat the same product is obtained.   In the first
process, the sulphuric acid decomposes the hydriodate of
soda existing in the saline matter; and not only disen-
gages the hydriodic acid, but decomposes it, a portion of
the oxygen of the sulphuric acid producing the abstraction
of its hydrogen and conversion into iodine; hence also a
formation of sulphurous acid.   In the other process the oxy-
gen from the oxide of manganese produces the same effect.
This method has the disadvantage, that in the decompo-
sition by the sulphuric acid, the sulphurous acid evolved,
aided by the aqueous vapour, re-acts on the iodine.   On
the other hand, if the muriatic acid has not been com-
pletely abstracted from the salt, the manganese has the
disadvantage of producing oxymuriatic gas, which acts on
it with as much energy.   From these circumstances the
product can scarcely be procured pure by the first volatili-
zation, and in general it contains a portion of sulphur.   It
is purified by distilling it a second time with a gentle heat
from a little of a weak solution of potash.   The crystals

may be freed from moisture by bibulous paper, and by slow sublimation may be obtained of a regular form.

The soapmakers' ley from kelp contains the hydriodate of soda or potash, and by boiling down, affords a salt which yields iodine in larger quantity than the salt from barilla. Different varieties of barilla and kelp yield very different quantities of it.

Iodine is a solid substance, of a greyish-black colour, with a lustre similar to that of plumbago. It is in the form of scales, or more regularly crystallized in rhomboidal plates, large and shining, or in slender lengthened octohedrons : its fracture is scaly, and its aspect somewhat greasy ; it feels soft and friable ; its odour is pungent, somewhat like that of chlorine weakened ; its taste is very acrid, and it stains the skin of a yellowish-brown colour : it is poisonous. Its specific gravity is 4.948. It seems to be a non-conductor of electricity, and in galvanic action it is attracted to the positive pole. Its combining weight is very high, being 155 on the scale of Wollaston. It suffers no change, Sir H Davy found, when voltaic sparks are taken in its vapour from ignited points of calcined charcoal.

Iodine melts at 225°, and under a common atmospheric pressure is volatilized at about 350. It rises with the vapour of water, and it may even in this way be volatilized at a lower temperature than 212°, but this is owing to the agency of the water favouring its vaporization. Its vapour is of a rich purple colour, a property by which it is eminently characterized, and from which Gay-Lussac derived its name. The deepness of this colour is more intense than that of any other vapour, and the specific gravity of the vapour appears to exceed considerably that of any elastic fluid. It is calculated by Gay-Lussac to be equal to 8.619.

It is soluble in water, but very sparingly, the water dissolving only about $\frac{1}{7000}$ of its weight: the solution ac-

quires an orange colour ; it destroys the vegetable colours, but with much less energy than oxymuriatic acid.

This substance is not inflammable, nor can it be combined with oxygen directly: it combines, however, with it in indirect methods, and forms an acid. It exerts no action on nitrogen, but a combination seems to be established between them by an indirect process by the action of ammonia, to be immediately noticed, and a detonating compound is formed. Hydrogen gas does not act on it at a common temperature, but if exposed to each other in a red hot tube, they unite, and a product is formed powerfully acid ; the same product is obtained more easily by the action of nascent hydrogen. Iodine and charcoal do not act on each other.

It unites with sulphur at a very moderate heat, forming a substance of a greyish-black colour and radiated texture, from which the iodine is again removed when it is distilled with water. Heated in sulphuretted hydrogen gas, it absorbs it in considerable quantity, and a reddish-brown liquid is formed, which, when water is added, becomes strongly acid, and deposites sulphur.

It combines with phosphorus even at the common temperature of the atmosphere, with the disengagement of heat, but, according to Gay-Lussac, without evolving light : the combination takes place in different proportions; one of phosphorus with eight of iodine form a compound of an orange colour, fusible at 212°, and volatile at a higher temperature; one with sixteen form a substance of a greyish-black colour, fusible at 84° ; one with twenty-four give a product of a black colour, partially fusible at 115° : these compounds are decomposed by water ; and it is by this mutual action that the acid which iodine forms with hydrogen is best obtained. With one of phosphorus and four of iodine, two substances are formed, the one apparently the same as that which is formed by the combination of one with eight, the other a reddish-

brown substance, containing scarcely a trace of iodine, and analogous to the red matter considered as oxide of phosphorus.

With the metals iodine in general combines : with some of them, as iron, zinc, or tin, at a low temperature, if the metal is divided. Though these combinations take place readily, they produce little heat, and seldom any evolution of light : that with potassium, however, is attended with much heat and light. These Iodurets, as Gay-Lussac names them, from their analogy to sulphurets, are destitute of metallic lustre ; they are of different colours, fusible, and in general by fusion assume a crystalline arrangement ; some of them, those particularly consisting of the more oxidable metals, are soluble in water, and at the same time decompose it, forming an acid with the iodine and an oxide with the metal. They are also decomposed by concentrated sulphuric acid, the metal is oxidated, and iodine is disengaged. In general, too, they are decomposed by oxygen at a red heat. And chlorine expels their iodine. Iodine itself and the oxides appear to have only weak attractions.

Iodine and the alkalis exert a mutual action, which is different in the dry and in the humid way, water being decomposed in the latter case, which modifies the results, the hydrogen forming one acid with iodine, the oxygen another, and each combining with the alkaline base. When passed in vapour over potash at a red heat, oxygen gas is disengaged, and ioduret of potassium is formed. When the iodine is submitted to the action of a concentrated solution of potash it dissolves speedily, a white granular precipitate is thrown down, which is an alkaline iodate of potash ; it is fused and decomposed by heat, giving results similar to those of the compound with the solid potash ; it deflagrates on burning charcoal. The liquor retains the compound of potash with the acid which iodine forms with hydrogen, with an excess of iodine,

which gives a yellow or brown colour. The action of soda is similar; barytes, strontites, and lime, seem to combine with iodine without giving out oxygen; their action with water is similar to that of the fixed alkalis, except that the compounds of these earths with the acid are of very sparing solubility.

The action of ammonia on iodine is more peculiar. When it is transmitted in the gaseous state over it, a viscid liquor of a brown colour and shining lustre is formed, which, as it becomes saturated with ammonia, loses its lustre and viscidity. This is an ioduret of ammonia; it has no fulminating property. When dissolved in water, decomposition of part of the ammonia takes place; the acid which iodine forms with hydrogen is produced; while the nitrogen of the decomposed ammonia unites with another portion of iodine; a brownish powder is produced; this detonates with a very gentle heat, or with a slight percussion, disengaging nitrogen and iodine. Gay-Lussac regards it as a compound of these, or an ioduret of nitrogen It is formed more easily merely by putting iodine in fine powder into liquid ammonia; from the violence of the detonations it produces, it ought to be prepared only in small quantity.

Iodine is separated from its combinations by sulphuric and nitric acids with little change: sulphurous acid gas does not act on it when dry, but diffused in water, sulphuric acid is formed, and the acid which iodine forms with hydrogen is produced. The sulphites and sulphuretted sulphites cause a similar decomposition of water with iodine, and a formation of hydriodic acid. The acid cannot be expelled in these cases from the sulphuric, for at the necessary temperature sulphurous acid is reproduced.

Dry iodine absorbs oxymuriatic gas rapidly, raising the temperature to 212°. The compound has a colour in some parts orange-yellow, in others red; both, according to Gay-Lussac, are compounds of chlorine with iodine; the

yellow, which contains the larger proportion, he names
Chloruret, the other Sub-chloruret of Iodine. They are
both deliquescent, and become dissolved on exposure to
the air; the solution of the chloruret is colourless when
the excess of chlorine is expelled; both solutions are
powerfully acid; they contain muriatic acid, and the acid
which iodine forms with oxygen, Iodic acid, as Gay-Lus-
sac names it; the salts of these acids being formed on add-
ing an alkali, and the only difference in the action of each
is, that from the solution of the sub-chloruret, a portion of
iodine is at the same time thrown down. As they destroy
the vegetable colours, they seem to contain oxymuriatic
acid, or at least retain the agency of that acid in the com-
bination. It might even be supposed, that the iodine and
chlorine form one compound, an acid possessed of this
property; that this acid is decomposed by the action of
an alkaline base, and resolved into the iodic and muriatic,
oxygen being communicated from the water to form the
one, and hydrogen to form the other, and that hence these
two acids are obtained in combination with an alkali from
the solution. Gay-Lussac adopts the first opinion, from
finding a similar product to be obtained by mixture of the
two acids. Sir H. Davy, on the contrary, has considered
the iodine as forming an acid by combination with chlo-
rine, which he has named Chlorionic Acid. As formed
by the sublimation of iodine in chlorine in great excess,
he describes it as a substance of a bright yellow colour,
which, when fused, becomes of a deep orange, and when
rendered elastic forms a deep orange-coloured gas. When
dissolved in water, and agitated in contact with chlorine,
it forms a colourless solution. It dissolves iodine in large
quantities, and thus forms coloured solutions.

Euchlorine gas is quickly absorbed by iodine; a bright-
orange colour is acquired, and a liquid is formed: when
the euchlorine is in sufficient quantity, a white substance
is produced: by the application of a gentle heat, the orange

compound of chlorine and iodine is volatilized, and a substance remains, which Sir H. Davy regarded as a compound of iodine and oxygen.   It is a white semi transparent solid, inodorous, and having a strong astringent sour taste : its specific gravity is such, that it sinks in sulphuric acid ; when heated strongly it melts, and by a stronger heat it is decomposed, and resolved into oxygen and iodine.

Iodine acts on some vegetable and animal substances. It in general gives them a brown stain.   It is soluble in alkohol and ether. Starch is a very delicate test of it when it is disengaged uncombined : a few drops of sulphuric acid detach it from any compound, and the iodine forms with the starch a compound of a very deep blue colour.   Its effect in tarnishing silver affords another delicate test.

Little certain is known with regard to the origin of Iodine.   The ashes of different sea-plants afford it : but except in those affording soda, the quantities are small, and often no traces of it can be discovered.   Sir H. Davy found, that when sea water free from any source of intermixture, by being taken at a distance from the shore, is evaporated, no distinct indications of iodine are obtained from it.   I have found, that common sea salt frequently contains it.   Mr Tennant has been said to have detected it in sea water ; but his method is not known.

Sect. II.—*Of Hydriodic Acid.*

Though hydrogen acts on iodine at an elevated temperature, and forms the acid which results from their mutual action, it is difficult to render the combination complete. It is obtained with more facility by indirect processes in which the hydrogen is presented in its nascent

state to the iodine. This is effected by submitting the compound formed by the union of phosphorus and iodine to the action of water ; a portion of the water is decomposed, its oxygen unites with the phosphorus forming phosphoric acid, and its hydrogen with the iodine forms hydriodic acid To obtain the proper result, an excess of phosphorus in the compound should be avoided; that composed of eight parts of iodine and one of phosphorus affords the best proportion ; and if this be moistened only slightly with water, the hydriodic acid, as it is formed, assumes the gaseous form. This acid may also be obtained by passing sulphuretted hydrogen gas through water in which iodine is diffused, the hydrogen is communicated to it, the sulphur is precipitated, and the hydriodic acid remains in solution. Sir H. Davy gave this acid the name of Hydrionic ; that of Hydriodic proposed by Gay-Lussac is preferable ; and considered simply as expressing the fact, that it is formed by the action of hydrogen on iodine, may be employed, whatever theory is held with regard to it.

This acid is permanently elastic. The gas is colourless ; its odour is similar to that of muriatic acid ; its taste is extremely sour ; its specific gravity is 4.443, air being 1 ; it is therefore one of the heaviest of the gases. 100 cubic inches weigh 135 grains.

When the gas is received over mercury it is decomposed ; iodine combines with the mercury, forming an ioduret of a greenish yellow colour, and hydrogen gas remains, equal to half the volume of the acid gas. This is considered as a proof of its composition, and from this result Gay-Lussac infers, that it is composed of equal volumes of the vapour of iodine and of hydrogen ; and by weight of 100 of iodine and 0.849 of hydrogen. In the opposite views the mercury must be supposed to combine with the radical of iodine and a certain proportion of oxygen, and the hydrogen is liberated.

Hydriodic acid suffers decomposition from other agents. Chlorine decomposes it by attracting hydrogen, and the purple vapour of iodine is immediately produced. It is also partly decomposed at a red heat: and with oxygen at this temperature suffers decomposition, water and iodine being the products

This acid gas is absorbed by water in large quantity, and forms a liquid which, when concentrated, is dense and smoking : it is not very volatile : what escapes from it when it is heated up to 255° is principally water ; above this the acid begins to rise ; at length the boiling temperature remains stationary at 262°.5 ; the specific gravity of the liquid is then 1.7, a degree of density which renders it a very powerful acid. When distilled it always becomes more or less coloured. It even suffers this change on exposure to the air, from partial decomposition, oxygen being absorbed, water formed, and a portion of iodine separated, which the acid dissolves so as to acquire colour.

Sulphuric, nitric and oxymuriatic acids decompose the liquid hydriodic acid; they attract its hydrogen, and the iodine is either precipitated, or rises in purple vapours. Chlorine, by producing this effect, is one of the most delicate tests to discover it, taking care to avoid adding an excess, by which the iodine would be retained dissolved, before the colour appeared. It suffers a similar change from the action of those oxides which impart oxygen readily, such as black oxide of manganese.

Hydriodic acid combines with the acids and earths, forming salts, named Hydriodates, which in general are soluble and crystallizable. Their solutions have all the property of dissolving iodine, and thus become of a reddish-brown colour ; it does not change, however, their state of neutralization ; they lose it when heated, or from exposure to the air. The greater number of them, when heated, or even when dried, are decomposed and converted into iodurets, or compounds of the metallic radical of the

base with iodine. Similar results are established in the action of the acid on the metallic oxides; and with regard to some of these, metallic iodurets are formed by precipitation, on adding an alkaline hydriodate to the metallic salt : they in general form dark coloured precipitates. Chlorine, nitric acid, and sulphuric acid decompose all the hydriodates, and precipitate iodine. Sulphurous acid, sulphuretted hydrogen, and muriatic acid at the usual temperature occasion no change. The history of these compounds belongs to that of their respective bases.

SECT. III.—*Of Oxiodic Acid.*

THE relation of chloric acid to chlorine obviously led to the conjecture, that an acid might be formed by the combination of oxygen and iodine. Their direct union cannot be effected; but Gay-Lussac inferred, that such a combination is established when iodine is acted on by an alkaline base with water : the water, he supposed, suffers decomposition; its hydrogen with one portion of iodine forms hydriodic acid, its oxygen with another portion forms this acid which he named Iodic Acid; and each of these acids remains combined with portions of the base. He endeavoured to procure the latter acid by adding sulphuric acid diluted to iodate of barytes; sulphate of barytes is precipitated; and the iodic acid combines with the water; but there always remained a small portion of sulphuric acid, and apparently a little barytes. The acid could be obtained only in combination with water, which Gay-Lussac considered as necessary to its existence in a free form. It may be concentrated so far as to become of

the consistence of syrup; its taste is extremely sour; light does not decompose it; when heated to 392° it is decomposed and resolved into iodine and oxygen; it is also decomposed by sulphurous acid and sulphuretted hydrogen, which attract its oxygen, and the iodine is precipitated: muriatic acid causes a production of oxymuriatic acid; sulphuric and nitric acids have no effect on it. Gay Lussac inferred its composition to be 100 of iodine with 32 of oxygen.

Sir H. Davy, it has already been remarked, had obtained, by exposing iodine to euchlorine gas, a product, which, when exposed to heat, allowed a portion of the substance which is formed by the combination of chlorine and iodine to be volatilized, and a white matter was obtained in which the iodine must retain the oxygen of the euchlorine, and which accordingly he considered as a compound of iodine and oxygen, and, in conformity to this, gave it the name of Oxy-iodine. It is probably the proper acid; though he considered it as acid only, when combined with water, and in this state proposed to name it Oxyiodic Acid. He has enumerated its principal properties in these two forms [*].

In the first it is a white semi-transparent solid; it has no smell, but a strong astringent sour taste. Its specific gravity is so considerable that it sinks in sulphuric acid. When heated strongly it is decomposed, undergoing fusion at the moment, and is entirely converted into gaseous matter and iodine. A heat about that of boiling olive oil is necessary for this. The gas disengaged is pure oxygen. In one experiment 3 grains lost .68.

This substance, though it remains unaltered in a dry atmosphere, deliquesces in humid air, and is very soluble in water; its solution first reddens and then destroys vegetable blues : it reduces other vegetable colours to a dull yellow. When its solution is heated, as the water is dis-

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[*] Philosophical Transactions, 1815, p. 203.

sipated, the liquid acquires the consistence of syrup, be-
comes pasty, and at length, by a stronger heat, yields the
solid matter unaltered. The paste is evidently a hydrate,
as it yields water in drying. If a sufficient heat is ap-
plied, a purplish tint is acquired, from the production of
iodine.

When heated with inflammable bodies, charcoal, sul-
phur, sugar, or the combustible metals, detonations are
produced. Its solution rapidly corrodes all the metals ;
both gold and platina are acted on, the first with most
energy. It combines with all the metallic oxides.

Its relation to the acids is singular. It appears to com-
bine with all the fluid or solid acids which it does not de-
compose. When sulphuric acid is added to its concen-
trated solution in hot water, a solid substance is precipi-
tated, which is a compound of the two; it may be fused,
forms rhomboidal crystals of a yellow colour, and when
decomposed by a strong heat, affords oxygen, iodine, and
sulphuric acid. The result with hydro-phosphoric acid is
similar: with hydro-nitric acid, white rhomboidal plates
are formed, which decomposed by heat afford this acid
with iodine and oxygen. Boracic acid is dissolved in it ;
the solution does not crystallize on cooling, but by eva-
poration, a solid white substance is obtained. By liquid
muriatic acid it is immediately decomposed, and the com-
pound of chlorine and iodine is formed. All these com-
pounds are strongly acid. When they are made to act
on alkaline bases, compounds of the respective acids and
of oxiodic acid are formed. These results, as Sir H. Da-
vy has remarked, explain the action of sulphuric acid, in
the production of the iodic acid of Gay-Lussac, and as-
sign the cause why a portion of the sulphuric acid al-
ways remains in that compound.

When a solution of the oxiodic acid is added to solu-
tions of the alkalis or alkaline earths, compounds are
formed, which Sir H. Davy considers as compounds of

oxygen, iodine, and metallic bases, and which he propos-
ed naming Oxyiodes. Gay-Lussac considers them as com-
pounds of iodic acid with the alkaline or earthy base, and
names them Iodates. Conformity to the analogy of the
established nomenclature would lead to their being named
Oxiodates, which name I shall employ. They are in ge-
neral decomposed at a red heat, giving out either oxygen
alone, or oxygen and iodine ; some of them deflagrate on
burning fuel; that of ammonia is fulminating; they are
dissolved in muriatic acid, forming oxymuriatic acid ; those
with alkaline bases are soluble and crystallizable; these
with the earths are less soluble and pulverulent ; those with
the metallic oxides are in general insoluble. They will
be noticed under their respective bases.

THE theory of the chemical relations of Iodine and its
compounds may be considered under different points of
view. As it has not been decomposed, the direct inference
is, that it is a simple body, which, with hydrogen, forms
hydriodic acid, and with oxygen oxiodic acid. And un-
der this view, the analogies which it has to chlorine serve
to confirm a similar doctrine with regard to the latter,
and, accordingly, it was the discovery of iodine chiefly
that favoured the new doctrine of chlorine.

Considering chlorine, however, as a compound of an
acid with oxygen, muriatic acid as a compound of the
same acid with combined water, and oxymuriatic as a com-
pound with an additional proportion of oxygen, the same
analogies would lead to similar conclusions with regard
to iodine and hydriodic and oxiodic acids. Or, accord-
ing to the view I have advanced, iodine may be a com-
pound of a radical with oxygen, oxiodic acid a compound
of the same radical with a larger proportion of oxygen,

and hydriodic acid a ternary compound of it with oxygen and hydrogen.

All the phenomena of these combinations may be explained with equal facility on any of these views; and although iodine is not proved to be a compound body, the weight of analogy is in favour of that conclusion, while, considering it as a simple substance, hypothetical assumptions are often required of the formation or decomposition of water, of the alkalies or earths, when there is no evidence of these exclusive of the hypothesis itself.

The analogies of iodine and chlorine are also very imperfect. The principal are its odour, its destroying colours, and its forming acids with hydrogen, and with oxygen. But its solidity, its weight, its insolubility in water, and comparative inertness, remove it to a very different class, and prevent nearly any strict conclusion being drawn from the one to the other.

The analogy between iodine and sulphur is perhaps greater, particularly in solidity, volatility, and insolubility in water, and it has the same important analogy of forming acids with hydrogen and with oxygen. But still it is defective; the inflammability of iodine constitutes a prominent distinction between them ; and the acid which it forms with hydrogen is altogether different in energy of action to that which sulphur forms with the same element.

The great weight of the combining quantity of iodine affords nearly a demonstration that it is a compound. And its specific gravity, colour, lustre, and the same qualities in many of its compounds lead to the conclusion, that it is of a metallic nature, probably a metal combined with oxygen. On this view, it may easily be conceived to form an acid by combination with hydrogen, and one more powerful by combination with oxygen and hydrogen. The properties of the bodies belonging to the class of metals are evidently more peculiar and diversified, the farther our knowledge of them is extended.

BOOK IV.

OF ALKALIS AND THEIR BASES.

An order of substances, possessed of important chemical
properties, has been distinguished by the title of ALKALIS.
Their characters are appropriate. They have an acrid
taste ; inflame or erode the skin, and dissolve animal mat-
ter, a property which has been named Causticity : they
exert a strong attraction to water : they change the blue
and green colours of vegetables to a green, the yellow to
a reddish-brown : they unite with oils and fats, forming
soaps : and they combine with the acids, and form com-
pounds, in which, when the combination is established in
certain proportions, the acid and alkaline properties are
mutually neutralized. Three alkalis have been long known
to chemists. One of them, from its volatility, has been
named Volatile Alkali ; to the other two the epithet Fixed
has been given. The volatile alkali has received the name
of Ammonia ; the others are named Potash and Soda.
Lately, some newly discovered bodies have been referred
to the same class.

Alkalis are distinguished as chemical agents, by pro-
perties the reverse of those of Acids. These two classes
are opposed in some measure to each other; in entering
into combination, the acids diminish the alkaline proper-
ties : the alkalis are equally subversive of the property of
acidity ; and when united in a certain proportion, the pro-
perties of neither appear in the compound.

There are other substances, however, besides the alkalis which act in opposition to acids, and neutralize the acid properties. The earths produce this effect, and with acids form compounds similar in their general properties to those which the alkalis form. The greater number of the earths possess even the characteristic alkaline properties, particularly that of changing the blue and purple colours of vegetables to a green. There exists, therefore, a strict analogy between these two orders of chemical agents.

This analogy is still farther extended. The metals when united with oxygen acquire the power of combining with acids, and of neutralizing the acid properties, forming compounds analogous to the compounds which the acids form with the alkalis and earths.

Thus, in the most important chemical character of these substances, that displayed in their relation to acids, Alkalis, Earths, and Metallic Oxides, are strictly connected; and the constitution of the last being known, analogy would have justified the conclusion, that the others are of a similar nature, or that the earths and alkalis consist of metallic bases combined with oxygen. This analogy was accordingly extended to the earths. It was often supposed that they are metallic oxides, and attempts were made to reduce them to the metallic form. But the same analogy does not appear to have been extended to the alkalis, or, if it were, it was only by a very remote and loose conjecture; and from the analogy of the composition of ammonia, which had been discovered to be a compound of nitrogen and hydrogen, it was rather inferred, that one or other of these elements was the alkaline principle.

At length the discovery of the real composition of the fixed alkalis was effected by the application of the powerful decomposing agency of galvanism. Sir H. Davy having submitted potash and soda to the action of a powerful galvanic battery, observed, that at the negative side, globules were collected, having metallic lustre, and at the

positive side a gas was disengaged, which he found to be oxygen. These results, he inferred, arose from the decomposition of the alkalis, which he in consequence regarded as compounds of the metallic substances thus obtained with oxygen. He submitted the earths to the same agency, and though their decomposition was less completely effected, results were obtained sufficient to authorise the conclusion, that they also are compounds of metallic bases with oxygen. And thus the whole series of substances capable of neutralizing acids, and so strictly connected in other general properties, were, with the exception of ammonia, proved to be of similar constitution, and to contain oxygen as a common element.

The analogy subsisting between ammonia and the other alkalis is so strict, and the anomaly which its constitution presents is so singular, that it has been very generally inferred by chemists that oxygen must exist in it as a constituent part; and as it is resolved by decomposition entirely into hydrogen and nitrogen gases, it has been farther inferred, that one or other of these must be a compound body, and contain oxygen as an ultimate element. These conclusions, however, rest on no evidence; and with the exception of this analogy, are supported even by no probable argument. Nor is there any proof of the existence of any metallic matter as its base.

The view which I have proposed of the chemical relations of oxygen and hydrogen to acidity may be extended to alkalinity, so as to remove this anomaly, without any hypothesis as to the constitution of ammonia. Oxygen exists as a constituent part of the greater number of acids, is their common element, and so far, therefore, may be regarded as a principle communicating acidity. There are acids, however, into the composition of which oxygen does not enter, and in which hydrogen is apparently the principle whence their acidity is derived. Now, as oxygen communicates alkalinity as well as acidity to bodies, so hy-

drogen may have a similar effect. Ammonia, in this point
of view, will fall to be regarded as a compound of which
nitrogen is the base, and hydrogen the alkaline principle.

Acidity is produced in a higher degree by the joint ac-
tion of oxygen and hydrogen, than by the operation of ei-
ther alone. A similar result, there is reason to conclude,
exists in their relation to alkalinity. The most powerful
alkalis, potash and soda, and the earths which have the
highest degree of alkaline energy, have been supposed to
contain water in considerable proportion, in intimate com-
bination, in their insulated form. But there is every rea-
son to draw the same conclusion with regard to this, as
with regard to the supposed presence of combined water
in the stronger acids. It is probable that the elements of
water rather exist in the combination. And thus the al-
kalis, applying the term in its most extensive signification
to denote those substances which neutralize acids, display
the same relations as acids; some being compounds of a
radical with oxygen; ammonia being composed of a radi-
cal with hydrogen, and potash, soda, barytes, strontites
and lime, (all of superior alkaline strength,) being ternary
compounds of a radical with oxygen and hydrogen.

Though a series is established from the alkalis and
earths to the oxides of the common metals, there are
grounds for regarding each of these orders as subdivi-
sions of a class, and for preserving distinctions between
them. Though the bases of all of them may be metallic,
those of the alkalis and earths have some peculiarities,
both in their physical and chemical properties, and it is
uncertain if they have yet been obtained in their state of
simplicity. And in their oxidated state, the alkalis, ex-
cept in the leading property of neutralizing the acids, and
forming saline compounds, are very different from the me-
tallic oxides, and are much more active in their chemical
agencies. The earths in some measure connect them, ha-
ving relations in properties with each.

Some of the earths approach so near in their general properties to the alkalis, that it has been proposed to transfer them from the one order to the other. Vauquelin made this change of arrangement with regard to two earths, barytes and strontites. There are sufficient reasons, however, for rejecting this innovation. Classes of substances, founded on agreement of properties, cannot be kept so distinct, but that a gradation from one to another may be traced; and wherever the limits are placed, there will be some room for objection. In the present case, ammonia at the extreme of the one class, and silica at that of the other, are substances very dissimilar, yet there is a series which connects them; and the gradation is such, that wherever we draw the line of distinction, the substances on either side may still be connected. It is preferable, therefore, to adhere to the division which has been established: if we were to deviate from it so as to transfer barytes and strontites to the alkalis, it would be difficult to assign a reason for not doing the same with lime; and if lime be received, magnesia might claim a place. The alkalis are distinguished, by their much greater solubility in water, and their stronger affinity to it, by their solubility in alkohol, in which the others are insoluble; by their greater fusibility and volatility; and, generally speaking, by greater activity in their chemical actions.

Two newly discovered bodies, I have stated, have been lately added to this class. One, to which the name of Lithina has been given, has been discovered in certain minerals. The other, Morphina, is extracted from opium. The latter appears to be exclusively a product of the vegetable system; and as I place the vegetable acids under the class of vegetable substances, this body is, on the same principle, to be referred to that class.

CHAP. I.

OF AMMONIA.

THE name of Volatile Alkali was given by the older chemists to a transparent liquid, which, in addition to the alkaline qualities, is volatile, and has an extremely pungent smell. This however is not the real alkali, but a solution of it in water. The former may be procured in a gaseous form, from this liquid, by the application of a moderate heat, as Priestley shewed; when collected over mercury, it retains this form at natural temperatures. To the pure alkali the name of Ammonia is given; its solution is named Liquid Ammonia, as by combination with water its properties are not materially altered.

Ammonia is a compound of nitrogen and hydrogen. Its composition, however, was not discovered from its formation; for when these two gases are mixed together, the elasticity of each is an obstacle sufficient to counteract their mutual affinity; nor can their combination even be effected as that of some other mixed gases can, by transmitting the electric spark through the mixture, or exposing them in any way to a high temperature.

The first observation leading to any knowledge of the composition of ammonia was made by Priestley. He observed, that on taking the electric spark or explosion in the gas over quicksilver, its volume is enlarged; until at length, by continuing the experiment, it occupies three times the space it before did. Its properties are also

changed; it is no longer absorbed by water, and is inflammable. A similar change was produced in it by transmitting it through a red-hot earthen tube. And he afterwards found, that by heating certain metallic oxides in it, they were reduced to the metallic state, water appeared, and the residual air seemed to be nitrogen gas *.

The theory of these experiments is now sufficiently evident. By the action of the electric spark, or of a red heat, the gas is resolved into its constituent elements, hydrogen and nitrogen; hence the enlargement of volume and change of properties †. The reduction of the metallic oxides is owing to the oxygen of the oxide combining with the hydrogen of the ammonia, and forming a small portion of water, the metal of course appearing in its metallic state; while the nitrogen, the other component principle of the alkali, being freed from its state of combination, assumes the gaseous form. Dr Priestley, however, did not draw from his experiments the just conclusion, or place the theory of them in a clear light.

Scheele likewise observed the decomposition of ammo-

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* Priestley's Experiments on Air, vol. ii, p. 389.
   Ibid. p. 396.

† A curious circumstance has been stated by Thenard, that the decomposition of ammonia does not take place so readily by transmission through an ignited earthen tube, as a metallic tube; and on inclosing in a porcelain tube a coil of metal, the decomposition of the ammonia, which had before gone on slowly and imperfectly, takes place rapidly. Yet the metal suffers no change, neither acquiring nor losing weight, nor exhibiting any alteration in its physical qualities. Iron, copper, silver, gold and platina, are the metals which have this property; the others do not possess it. No very satisfactory explanation can be given of this; but if fully established. it must apparently depend on some effect from the conducting power of the metal in imparting temperature, or perhaps on some electrical relation. (Annals of Philosophy, vol. i, p. 392.)

nia, and the production of nitrogen gas, particularly in the detonation of a preparation named Fulminating Gold, a compound of ammonia and oxide of gold *; and Berg- man gave a theory of this, on the supposition that the am- monia is decomposed †.   Both these chemists regarded it as a compound of phlogiston and nitrogen, without affix- ing perhaps a precise idea to the former term.

Berthollet first communicated precise ideas on the na- ture of ammonia, by comparing the experiments of Priest- ley and Scheele, and instituting others.   In decomposing the salt formed by the union of ammonia with nitric acid by heat, he found, that a quantity of water is obtained, which did not pre-exist in the salt : he inferred, therefore, that this water had been formed in the decomposition, and that the hydrogen, which is one of its constituent parts, is derived from the ammonia.   Again, having observed, that when oxymuriatic acid, which yields oxygen readily, is add- ed to liquid ammonia, an effervescence takes place, from the evolution of nitrogen, he concluded, that the oxygen of the acid combines with the hydrogen of the ammonia, and forms water ; and the nitrogen gas disengaged he re- garded as its other constituent principle.   Hence, from the two experiments he inferred, that hydrogen and nitro- gen are the component parts of this alkali ; and on this theory, found it easy to give an explanation of the expe- riments of Priestley and Scheele.   He farther endeavour- ed to determine the proportions of the elements of ammo- nia.   The experiment which he regarded as affording the most accurate result, was that of decomposing the ammo- niacal gas by the electric spark ; — it was thus resolved in- to its two constituent gases ; — a quantity of oxygen was then added in the eudiometer of Volta ; and by detona- tion the oxygen combining with the hydrogen, water was

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* Treatise on Air and Fire, p. 141.
† Chemical and Physical Essays, p. 159.

formed, and the nitrogen remained. From this experiment he concluded, that in ammonia, 121 parts by weight of nitrogen are combined with 29 of hydrogen, or in 100, 80.7 with 19.3 [*].

It was found difficult to confirm the composition of ammonia by synthesis; the two gases not combining, even when the electric spark is taken in their mixture. It had been observed, however, by different chemists, that in some experiments, ammonia appeared to be produced, where it did not pre-exist in the materials. These were repeated and diversified by Dr Austin, who ascertained the principle on which their success depends.

In presenting two gases to each other, the obstacle to the effective exertion of their mutual affinity is the elasticity of each. If therefore they meet when disengaged from substances in which they exist, before they have fully assumed the elastic form, their union may take place. This Priestley termed the action of gases in their *nascent state :* and it is well exemplified in the formation of ammonia. Thus it had been known, that in the action of nitric acid on tin, ammonia is formed, and the application of this principle easily explained this. Nitric acid is a compound of oxygen and nitrogen, and it contains also a portion of water. Tin is a metal which has a strong attraction to oxygen, and is capable of combining with a large quantity of it; it attracts therefore oxygen both from the acid and the water; and the nitrogen of the one, and hydrogen of the other, being disengaged, and meeting in their nascent state, unite and form ammonia.

Dr Austin repeated this and other experiments, and diversified them so as to establish the circumstances requisite for the formation of this compound. He found that it was not necessary that both the gases should be in this state; but that if nascent hydrogen were presented

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[*] Mémoires de l'Acad. des Sciences, 1785, p. 316.

to gaseous nitrogen, ammonia was formed.   In a tube, containing nitrogen gas, inverted in quicksilver, he put a small quantity of iron-filings, moistened with water ; in twenty-four hours a sensible portion of ammonia was formed, the iron attracting the oxygen of the water, and the hydrogen at its disengagement combining with the nitrogen.   The experiment even succeeds in atmospheric air, though a longer time is requisite ; and hence a source of fallacy attending the use of iron-filings and sulphur, moistened, as a eudiometer, part of the nitrogen being abstracted, to which Dr Austin ascribes, with probability, the great diminution which Scheele observed, of atmospheric air from such a mixture—amounting to 27 or 28 in 100 parts.

The experiment does not succeed when the circumstances are reversed, and nascent nitrogen is presented to gaseous hydrogen.   This Dr Austin tried by mixing hydrogen gas with nitrous gas,—a compound of oxygen and nitrogen, and exposing the mixture to iron-filings ; the iron attracts the oxygen of the nitrous gas, and disengages the nitrogen ; but this, though in contact with hydrogen gas, does not combine with it ; a difference of result which he ascribes to the great rarity of hydrogen gas, the particles of which are at such distances, that the particles of nitrogen are unable to exert that affinity which becomes effective when the hydrogen is in a denser state *.

After the discovery of the existence of oxygen in the fixed alkalis, analogy led to the conclusion, that oxygen must also be an element in the composition of ammonia ; and its analysis not having been executed with a view to this, it was supposed that this oxygen might be contained in the elastic fluid obtained in the decomposition, or that a little water might be deposited.   Sir H. Davy, therefore, submitted ammonia to analysis, with the view of determining this.   In its decomposition by electricity, the

* Philosophical Transactions, vol. lxxviii, p. 379.

weight of the nitrogen and hydrogen gases obtained ap-
peared to be less than that of the ammonia decomposed,
which he inferred to be owing to the existence of oxygen
in the alkali, part of which combined with hydrogen form-
ing water, and part with the platina wires employed in
the electrization.   Having transmitted ammoniacal gas
over iron-wire ignited in a platina tube, to each extremi-
ty of which a glass tube was adapted, kept cold by a freez-
ing mixture, no moisture was deposited in the one which
conveyed the gas, but in the other through which it pass-
ed after decomposition, moisture was evident, and the gas
appeared densely clouded : the iron-wire too was found to
be superficially oxidated, and had gained in weight $\frac{44}{100}$
parts of a grain.   And, lastly, when charcoal was ignited
in very pure ammoniacal gas by a galvanic battery, a great
expansion of the aërial fluid took place, and carbonate of
ammonia was formed.   From all these results, he infer-
red, that oxygen exists in ammonia,—that the quantity
cannot be estimated at less than 7 or 8 parts in the hun-
dred, and that it may even exceed this *.

The researches of other chemists have shewn, however,
that these results had been incorrect.   Dr Henry submit-
ted ammonia to the action of electricity, in an apparatus
so constructed, that the only metallic surface exposed to
the gas consisted of the sections of two platina wires, each
$\frac{1}{50}$ of an inch in diameter, inserted in the glass tube, seal-
ed hermetically, and ground down so that the points only
were exposed.   No oxygen could be discovered in the elas-
tic fluid into which the ammoniacal gas was resolved by de-
composition.   Neither could the smallest quantity of mois-
ture be discovered, during or after the agency of electricity
in decomposing ammonia.   The gas, after careful desicca-
tion from the action of potash, shews no signs of conden-
sed moisture when exposed to a cold of 0° of Fahrenheit ;

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* Philosophical Transactions, 1808.

and when decomposed by electricity if care has been taken that no humidity has been communicated to it in transmission through mercury or from any other source, no signs of moisture are exhibited at a temperature of 20° of Fahrenheit, and the smallest perceptible traces at a cold of 0°. The appearance of moisture, therefore, in former experiments, Dr Henry concluded, had been derived from some extraneous source [*].

The same question engaged the attention of the younger Berthollet. Ammonia, by the action of electricity, he found to be resolved into hydrogen and nitrogen gases alone, without any trace of oxygen; and the weight of these corresponded to the weight of the ammonia decomposed. The same result was obtained in its decomposition by heat; in neither case was there any deposition of moisture, and when the decomposition was effected in both modes with iron wire in contact with the gas, the metal did not suffer any oxidation [†].

It follows from these experiments, that no oxygen can be discovered in the composition of ammonia. Some weight, however, has still been supposed due to the inference from analogy, that it must contain oxygen, and on this supposition it must be inferred that either hydrogen or nitrogen must be a compound, and contain oxygen as a constituent element. Hydrogen may from its properties be inferred to approach nearest to the elementary state. Nitrogen has, therefore, been supposed to be compound. And Berzelius has assigned the quantity of oxygen from the principle established by Richter,—that all metallic bases saturating the same quantity of an acid, must contain the same portion of oxygen combined with them. The proportion of oxygen in ammonia from this principle must be 47 in 100 parts; and this he considered as existing in ni-

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[*] Philosophical Transactions, 1809, p. 130.

[†] Mémoires d'Arcueil, t. ii, p. 268. Nicholson's Journal, vol. xxiv, p. 374.

trogen, giving the proportion in its composition at 55.6 in
100. Berzelius added some other analogical arguments
to strengthen this conclusion. It is scarcely necessary to
say, that it has no support from any experimental investi-
gation *.

The analogy in chemical constitution between ammonia
and the other alkalis, appeared to be confirmed under an-
other point of view,—that of its base being of a metallic na-
ture. The experiment whence this was inferred, consists
in placing quicksilver in contact with ammonia in the gal-
vanic circuit; it increases in volume, becoming thick, and
at length nearly concrete, but retaining its metallic lustre.
The experiment was first made by Dr Seebeck of Jena,
by placing carbonate of ammonia, slightly moistened in
communication with the positive pole, placing a globule of
mercury upon it, so that the mercury is in communication
with the negative side †. Berzelius and Pontin made the
experiment with a similar result, with a solution of pure
ammonia. Sir H. Davy diversified the experiment, and
found the amalgam to be more readily produced when mu-
riate of ammonia is employed. The globule of quicksilver
increases to about five times its original dimensions, me-
tallic crystallizations shooting from it : at 70 or 80° of
temperature it remains soft, of the consistence of butter ;
at 32° it becomes harder, and forms a crystallized mass, in
which facets appear : its specific gravity is below 3. He
obtained a similar product by employing the agency of
potassium or sodium, either of these bodies being combin-
ed with quicksilver, and made to act on muriate of am-
monia ; enlargement of volume took place to six or seven
times the original bulk, and the compound seemed to con-
tain more ammoniacal base than that procured by elec-

* Nicholson's Journal, vol. xxx, p. 266. Annals of Philo-
sophy, vol. ii, p. 364.
          † Annales de Chimie, t. lxvi, p. 191.

tricity. He farther found, after the Swedish chemists, that the ammoniacal amalgam thrown into water yields ammonia, and evolves hydrogen in volume equal nearly to half its own; and when it is confined in a given portion of air, the volume of the air is enlarged, from the production of ammoniacal gas, equal to one and a half, or one and three-fifths of the volume of the amalgam, while a quantity of oxygen equal to one-seventh or one-eighth of the ammonia disappears, quicksilver being also reproduced *.

The changes which the quicksilver suffers in this experiment are similar to those which it would suffer from combination with a metal: they seem, therefore, to justify the conclusion, that metallic matter is communicated from the ammonia. Berzelius and Pontin, accordingly, inferred from the experiment that ammonia is of similar constitution with the fixed alkalis,—a compound of a metallic base with oxygen; that from the influence of voltaic electricity it is decomposed, and, in conformity to the usual law, its oxygen is attracted to the positive side, and its metallic base to the negative, where it combines with the quicksilver. And this appeared to be inferred by the facts, that when the ammoniacal amalgam is dropt into water, it returns to the state of quicksilver, ammonia is reproduced, and hydrogen is evolved,—changes which they ascribed to the decomposition of a portion of water, and the combination of its oxygen with the ammoniacal metallic base. To this supposed base the name of Ammonium has been given. It must of course be held to be a constituent either of hydrogen or nitrogen.

All attempts, however, to separate this supposed substance from the quicksilver, and obtain it insulated, have been unsuccessful. Whether the amalgam be allowed to suffer spontaneous decomposition, or be decomposed by heat, the products are, ammonia, hydrogen and quicksilver.

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* Philosophical Transactions, 1808.

A different view of this difficult subject has therefore been given by Gay-Lussac and Thenard *. They consider the ammoniacal amalgam as a compound of quicksilver, with small portions of hydrogen and ammonia. In its formation, therefore, they suppose, that the water of the moist ammoniacal salt is decomposed; its oxygen is attracted to the positive galvanic pole; its hydrogen passes to the negative side; the ammonia is also, in conformity to the usual law, attracted to that side, and by this influence of electricity, aided perhaps by a weak chemical affinity, the hydrogen and ammonia are combined with the quicksilver. In entering into this combination, they probably suffer a very slight degree of condensation, the affinity by which they are combined being so weak, that they again escape, when the electrical influence is suspended; they must therefore add greatly to the volume of the quicksilver, and of course diminish its specific gravity, and hence the great levity of the ammoniacal amalgam. Its metallic qualities are of course to be considered as derived from the quicksilver.

The phenomena which occur in the formation of this substance are favourable to this opinion. There is an evolution of oxygen and of the acid of the salt at the positive pole, while at the negative side there is scarcely any effervescence; but if the quicksilver be removed, there is a brisk effervescence, which must be ascribed to the decomposition of the water present. This decomposition must have equally taken place when the quicksilver is present, and since no hydrogen is then evolved, the conclusion seems to follow, that it enters into combination with the quicksilver, and of course into the composition of the amalgam. Its production by the medium of potassium must be ascribed to the potassium attracting the oxygen

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* Recherches Physico-Chimiques, tom. i, p. 52.

of the water present, while the hydrogen and a portion
of ammonia combine with the mercury.   And it deserves
remark, that the amalgam can be formed in either mode
only with a humid ammoniacal salt, and cannot be form-
ed in ammoniacal gas ; water therefore is essential to its
formation, probably by affording nascent hydrogen.

The results from its decomposition are not less favour-
able to this opinion.   The evolution of hydrogen, when
it is dropt into water, is owing to the escape of the hydro-
gen from it, and not to the decomposition of water ; and
the presence of water, or of oxygen, is not necessary for
its decomposition.   The separation of its constituents is
effected with the greatest facility.   Gay-Lussac and The-
nard found, that if put into a narrow glass flask perfectly
dry and full of air, and agitated for a few minutes, quick-
silver is reproduced, and ammonia and hydrogen evolved,
while the air loses none of its oxygen.   The ammoniacal
amalgam formed by the medium of potassium is decom-
posed with equal facility when it is diffused in an addition-
al portion of quicksilver to remove any excess of potassium,
and the same products are evolved.   The conclusion which
follows is, that the amalgam is a compound of quicksilver,
hydrogen and ammonia; for it is resolved into these with-
out the agency of any other substance.   Did it consist, ac-
cording to the opposite opinion, of the de-oxidated base
of ammonia, oxygen must be necessary to the reproduc-
tion of the ammonia from it.   But whence is this oxygen,
as Gay-Lussac remarks, to be derived ? none is abstract-
ed from the air, and water is not present to afford it.

All that can be opposed to this is the difficulty of free-
ing entirely the ammoniacal amalgam from water ; and
Davy maintained, that it is from this source that these re-
sults are obtained.   Gay-Lussac and Thenard appear to
have obviated this in a satisfactory manner.   They remove
the external surface of the amalgam after it has been pro-

duced, take only the central part, and introduce it into a very dry jar over dry mercury, and immediately in decomposing, it gives out ammoniacal and hydrogen gases. To make the experiment with still more precision, they prepared the amalgam by the medium of potassium, took out the interior part with a very dry iron spoon, and put it into a tube almost full of mercury, which had been previously boiled; having closed the tube thus filled with mercury and the amalgam by a very dry stopple, it was inverted in mercury, also well dried. The amalgam rose above the mercury, and was almost immediately decomposed by a slight agitation, with the same evolution of ammoniacal and hydrogen gases. Here every precaution was taken to exclude humidity: that it adhered to the mercury or the vessels can scarcely be supposed, and that it did not, was proved by no gas being evolved when an amalgam of potassium, instead of an amalgam of potassium and ammonia, was introduced. The interior part of the ammoniacal amalgam could not be supposed to contain humidity, for the presence of water is incompatible with the existence of potassium; and the external part could be removed with perfect facility. The experiment therefore appears conclusive [*].

Gay-Lussac and Thenard endeavoured also to determine the quantities of hydrogen and ammonia combined with the quicksilver in this substance. In the elastic fluid produced in its decomposition, the ammonia is to the hydrogen as 28 to 23 ; from the quantity of hydrogen given out by the amalgam, it is inferred, that the quicksilver in passing into that state absorbs 3.47 times its volume of that gas: the quantity of ammoniacal gas it absorbs is therefore equal to 4.22 times its volume ; hence the quick-

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[*] Recherches Physico-Chimiques, tom. i, p. 63. Nicholson's Journal, vol. xxix, p. 61.

silver, in being converted into this amalgam, must gain about 0,0007 of its weight *.

From the preceding account of the composition of ammonia, it appears that it stands isolated with regard to the other alkalis, and probably with regard to all salifiable bases. They consist of metallic bodies combined with oxygen ; but there are no grounds from any experimental evidence, on which it can be inferred, either that oxygen exists in its composition, or that it contains metallic matter. This singular anomaly is removed without any hypothetical assumption, by the view I have proposed, (already briefly illustrated, p. 511.) in considering hydrogen as an alkaline principle. Oxygen confers on some bodies in combining with them acidity, on others alkalinity. Hydrogen likewise communicates in some cases the former property ; there is therefore every reason to conclude that it may also communicate the latter, a conclusion which is more probable, from the consideration, that oxygen and hydrogen, by their joint action, produce acidity more powerful than arises from the operation of either alone ; and that in the constitution of the fixed alkalis, they observe the same law, giving the alkaline power in a higher degree than is produced by the action of oxygen alone. Ammonia, therefore, is an alkali, of which nitrogen is the base, and hydrogen the alkaline principle ; and in this respect it bears the same relation to the other alkalis, that sulphuretted hydrogen does to the acids.

There has been considerable discordance in the estimate of the proportions of nitrogen and hydrogen which form ammonia; and it is singular, that in experiments which appear to have been conducted with much care, there should have been so much diversity in the results. Berthollet had found the volume of ammoniacal gas to be nearly doubled,

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* Recherches Physico-Chimiques, tom. i, p. 72. Nicholson's Journal, vol. xxix, p. 380.

by decomposition 100 measures being expanded to 194,
and 100 measures of the expanded gas he found to be com-
posed of 72.5 of hydrogen, and 27.5 of nitrogen, whence
he inferred, that ammonia consists of 80.7 of nitrogen,
and 19.3 of hydrogen by weight. Davy stated that 100
measures of ammonia are enlarged by decomposition to
from 180 to 185; and these, in 100 parts, consist of 74 of
hydrogen and 26 of nitrogen by measure. Dr Henry,
obtained results nearly corresponding with Berthollet's,
100 measures being converted into 198.78. But in repeat-
ing the experiment with additional precautions the quick-
silver being boiled in the tube, and remaining hot when
the gas is passed through it, the result was nearly the same
as Davy's, 100 measures expanding into 180.6, and 100 of
these consisting of 73.75 hydrogen, and 26.25 nitrogen.
These results were confirmed, though not with perfect uni-
formity, by another mode of analysing ammonia, that of
detonation with oxygen. He found that within the limits
of three volumes of oxygen to one of ammonia, and three
of ammonia to 1.4 of oxygen, the mixture detonates from
the electric spark. If the oxygen gas exceed considerably
the ammonia, the latter disappears entirely; the residue is
nitrogen with the redundant oxygen; but a portion of ni-
tric acid is also formed, which introduces a source of error.
If the ammonia exceeds considerably the oxygen, no for-
mation of acid takes place, and although the proportion of
oxygen may not be sufficient to combine with the whole
hydrogen, the entire quantity of ammonia is decomposed;
the oxygen combining in the detonation with part of the
hydrogen, and the remaining hydrogen with the nitrogen,
forming a mixture which, by the addition of a new quan-
tity of oxygen, may be inflamed by the electric spark:
The quantity of hydrogen may thus be estimated from the
quantity of oxygen consumed. The results by this me-
thod were not perfectly uniform, but Dr Henry considers
the lower number as most correct, the proportion of 183.3

of gas produced from 100 of ammoniacal gas. The proportions too of hydrogen and nitrogen in this gas were not altogether uniform, but varied from 72 of hydrogen and 28 of nitrogen, to 73.9 and 26.1.

The proportions by A. B. Berthollet differ considerably from these. 100 measures of ammonia he found increase by decomposition to 204 : and the proportions of hydrogen and nitrogen in these in volume are 75.5 to 24.5. Mr Dalton from some experiments inferred, that 100 measures. of dry ammonia do not give less than 185 or 190 measures by decomposition, and that the proportion of hydrogen and nitrogen gases in this are by volume 72 and 28,—results which agree nearly with the original experiments of the elder Berthollet, made without any theoretic views as to the quantities *. The difference in all these experiments is principally to be ascribed to the difficulty of entirely excluding moisture, which at first condenses a little ammonia, and as the decomposition proceeds gives it out again, so as to render the quantity decomposed greater than what it appears to be, and therefore increases the quantity of elastic fluid produced. On the other hand, it is possible that a little ammonia may escape decomposition, and from this the enlargement of volume may not appear so great as it actually is. Mr Dalton has remarked, that in the detonation with oxygen, whatever proportion be used, a little nitrogen may be consumed with the hydrogen. Taking the proportions assigned by A. B. Berthollet, they are almost exactly those of 3 volumes of hydrogen and 1 volume of nitrogen : and the accuracy of these is perhaps rendered more probable by their being conformable to the law observed in the combinations of elastic fluids,—that they unite in simple proportions estimated by their volumes. Converting them into proportions by weight, 100 of ammonia will consist of 81.5 of nitrogen and 18.5 of hydrogen, proportions differing little from those originally

* Chemical Philosophy, p. 432.

assigned by the elder Berthollet. From the comparative specific gravities, the condensation attending the combination is equal to half the volume of the whole gases, or twice the volume of the nitrogen; and hence, when ammoniacal gas is decomposed by the electric spark, and converted into hydrogen and nitrogen gases, it is doubled in volume.

AMMONIA cannot be formed in any considerable quantity by the direct combination of its constituent principles. It is produced by indirect processes, and usually from the decomposition of animal substances by heat. If bones be exposed to heat in an iron still, this formation of ammonia takes place, from the combination of portions of the hydrogen and nitrogen of the animal matter contained in the bone. There is also formed, from other combinations of the principles of the animal matter, a quantity of carbonic acid, with which the ammonia unites; and this compound is obtained partly solid, and partly dissolved in a portion of water which distils over, forming what were named the salt and spirit of Hartshorn *. Other animal substances furnish it, as do also some varieties of vegetable matter. The soot of coal, which is of vegetable origin, yields it combined with some of the acids.

The ammonia obtained by such processes is mixed with an empyreumatic oil, which gives it a fetid odour. To free it from this, the ammonia is combined with an acid; and the ammoniacal salt is obtained by evaporation in a solid state. A process of this kind, afterwards to be de-

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* Dr Woodhouse has affirmed, that the product of ammonia is five times greater, when this process is performed in an apparatus into which the air is admitted, than when it is excluded, owing, as he supposes, to the nitrogen of the atmosphere combining with hydrogen from the bones. Philos. Mag. vol. vii, p. 86.

scribed, is carried on, on a large scale, to obtain a salt used in large quantities in some of the arts,—the muriate of ammonia, or sal ammoniac of commerce ; and the chemist, instead of following the different steps now stated, avails himself of this salt to obtain pure ammonia.

One part of it is reduced to powder, and mixed in a retort with two parts of newly slaked lime On applying heat, the ammonia is disengaged in the elastic state, the lime dislodging it by combining with the muriatic acid, which is the other ingredient of the muriate of ammonia. As the ammoniacal gas is largely absorbed by water, it must be received in jars filled with quicksilver.

As it is inconvenient preserving and using it in this form, it is, for common purposes, used condensed by water, forming what is named Liquid Ammonia : This is prepared by connecting a retort containing the mixture of muriate of ammonia and lime in the above proportions, and about thrice their weight of water, with the bottles of Woolfe's apparatus containing water. The retort being placed in a sand bath, and a moderate heat applied, the ammonia is expelled, part of it is condensed in the first bottle by the water which distils over, the rest is absorbed by the water in the other bottles. An improvement in the process has been introduced into the London Pharmacopœia. About equal weights of muriate of ammonia and slaked lime are mixed with four times the weight of the mixture of warm water ; the mixture is agitated ; after cooling, the clear liquor is drawn off, and distilled in a retort, about a fourth of it being drawn off by distillation. The inconvenience of the large mass of lime in the retort, and the difficulty of afterwards removing the residue, are thus avoided, while a sufficient quantity of lime enters into combination with the acid and ammonia to retain the acid, and allow the ammonia to escape when the heat is applied.   In the large way, the distillation is usually performed in an iron still, a larger proportion of water being

added, and this being condensed by being passed through
a tube placed in a refrigeratory, and terminating in a range
of receivers.

Ammonia, at any temperature above —56° of Fahren-
heit, exists when uncombined in the gaseous form.   At
that temperature, according to Guyton *, it becomes li-
quid, but this is probably principally from the operation
of the hygrometric vapour it contains.   This hygrometric
vapour is abstracted from it entirely with great difficulty.
Its specific gravity at 60° of Fahrenheit is 0.000715.   It
is to that of atmospheric air as 590 to 1000.   100 cubic
inches weigh, according to Kirwan, 18.2, according to
Davy 18.4, according to Biot and Arago 19.6 grains. Its
smell is extremely pungent; it inflames the skin, and ani-
mals are immediately killed by immersion in it.

Ammonia in its gaseous state is inflammable, and this
property of inflammability distinguishes it from all the
other substances possessed of alkaline properties.   When
a kindled match is immersed in it, the flame, before it is
extinguished, is enlarged, and is of a pale yellow colour at
the edges ; if mixed previously with two-thirds of atmos-
pheric air, it kindles, and gives a white lambent flame. It
detonates with oxygen gas.   The circumstances connect-
ed with this combustibility of ammonia have been ascer-
tained with more precision by Dr Henry, in his experi-
ments on its analysis already referred to †.   The detona-
tion is effected only when the two gases are in a certain
proportion.   With a greater proportion of oxygen gas
to ammonia than that of three to one, or of ammonia to
oxygen than that of three to 1.4, the mixture does not in-
flame.   But within these limits it is inflamed readily by
the electric spark.   The results are different according to
the proportion.   If the volume of oxygen gas be double

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* Annales de Chimie, t. xxix, p. 279.
† Philosophical Transactions, for 1809.

that of the ammonia, the latter is entirely consumed, its hydrogen combines with the requisite quantity of oxygen forming water, and its nitrogen partly remains with any redundant oxygen, and is partly combined with a portion of oxygen forming nitric acid, which, uniting with ammonia, forms a dense vapour. If the ammonia exceeds considerably the oxygen, no nitric acid is formed: if the proportion of oxygen is that which is just necessary to saturate the hydrogen, nitrogen remains; but if the proportion be even lower than this, still the whole of the ammonia is decomposed, part of its hydrogen combines with the oxygen, and the remaining hydrogen, with the nitrogen, form a mixture, which on the addition of a fresh quantity of oxygen may be inflamed by the electric spark. No mixture of ammonia with atmospheric air in any proportion can be inflamed by the electric spark: but the mixture of it with oxygen, even when diluted with six times its bulk of atmospheric air, burns. Ammonia introduced from a small aperture in a tube into oxygen gas, suffers slow combustion, burning with a pale yellow flame. Nitrous oxide and nitric oxide gases form mixtures with ammonia which are capable of being inflamed.

Ammonia is decomposed likewise by oxymuriatic gas; its hydrogen acting on the latter forms muriatic acid, with which a portion of ammonia combines, and its nitrogen is liberated. If the two gases are dry, the mutual action is attended with inflammation. Oxymuriatic gas transmitted through the aqueous solution of ammonia likewise decomposes it. Iodine, it has been stated, decomposes ammonia, forming hydriodic acid and ioduret of nitrogen.

Ammonia has a strong attraction to water. In its gaseous state it retains a little in solution, which appears when the gas is intensely cooled. This water is, however, completely abstracted by exposure to potash, so that it affords no trace of it even when resolved into its elements, as Henry and the younger Berthollet found. By water,

the gas is absorbed with rapidity. Below 50° the wa-
ter takes up rather more than one-third of its weight of
the gas. The specific gravity of the liquid is diminished
by the absorption, being, when saturated, not more than
9054. Mr Dalton found, that at 50° of Fahrenheit wa-
ter will absorb at the maximum 419 times its volume of
the gas; but it retains this only when under the pressure
of ammoniacal gas: if exposed to the atmosphere, or if
the incumbent gas have an intermixture of atmospheric
air equal to $\frac{7}{8}$ths of the volume, the water does not retain
more than 162 times its volume. The saturated solution,
according to Vauquelin, crystallizes at —40°; and con-
cretes into a jelly, losing its odour, at —58°.

The following tables shew the proportions of ammonia
in solutions of different specific gravities. The first is by
Mr Dalton; the second by Sir H. Davy: they do not,
however, altogether correspond. The numbers marked
by an asterisk in the latter table were found by experi-
ment; the others by calculation; and in the former, those
with the proportions of ammonia above the specific gravi-
ty of .94 were in part determined in the latter mode.

Specific Gravity.	Grains of Ammonia in 100 water-grain measures of liquid.	Grains of Ammonia in 100 grains of liquid.	Boiling point of the liquid in degrees of Fahrenheit.	Volume of gas condensed in a given volume of liquid.
..850	50	35.5	26°	494
.860	28	32.6	38°	456
.870	26	29.9	50°	419
.880	24	27.3	62°	382
.890	22	24.7	74°	346
.900	20	22.2	86°	311
.910	18	19.8	98°	277
.920	16	17.4	110°	244
.930	14	15.1	122°	211
.940	12	12.8	134°	180
.950	10	10.5	146°	147
.960	8	8.3	158°	116
.970	6	6.2	175°	87
.980	4	4.1	187°	57
.990	2	2.	196°	28

100 parts of Specific Gravity.	Of Ammonia.	100 parts of Specific Gravity.	Of Ammonia.
.8750*		.9455	14.53
.8875		.9476	15.46
.9000		.9513	12.40
.9054*	32.5	.9545	11.56
.9166	29.25	.9573	10.82
.9255	26.00	.9597	10.17
.9326	25.37	.9619	9.60
.9385	22.07	.9692*	9.50

Note: The "contain" labels appear vertically between the first and second columns, and between the third and fourth columns. Ammonia values: 32.5, 29.25, 26.00, 25.37, 22.07, 19.54, 17.52, 15.88

Ammonia exerts scarcely any action on the simple inflammables. By charcoal it is merely mechanically absorbed; on phosphorus it produces no effect, its relations to sulphur, however, and sulphuretted hydrogen are more peculiar.

Thenard states, that when sulphur and ammoniacal gas are transmitted through an ignited porcelain tube, hydrogen and nitrogen gases are disengaged, and a large quantity of a crystallized product is deposited, which is sulphuretted hydro-sulphuret of ammonia [*].

When equal volumes of sulphuretted hydrogen and ammoniacal gases are mixed together, a dense white vapour is produced; they are almost completely condensed, and a thin soft deposite is formed on the sides of the vessel, which exhales a penetrating vapour when exposed to the air [†]. This appears to form the proper HYDRO-SULPHU-RET OF AMMONIA. Thenard states, that if the vessel in which the two gases are mixed, be surrounded with ice, the compound condenses in crystalline needles, which are white while the air is excluded, but become yellow when exposed to it, probably by decomposition and the formation of a sulphuretted hydro-sulphuret. The hydro-sulphuret is, however, so volatile, that it rises to the upper

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[*] Annales de Chimie, t. lxxxiii, p. 132.
[†] Philosophical Transactions, vol. lxxvi, p. 136.

part of the vessel and condenses in crystals, leaving the compound with excess of sulphur. Another combination is established by passing a current of sulphuretted hydrogen gas through a solution of ammonia in water; a great part of it is absorbed, the colour becomes of a yellowish-green, and the liquid acquires a fetid odour. This forms what has been named Hepatized ammonia. The ammonia in it does not appear to be neutralized; and is probably in the state of sulphuretted hydro-sulphuret.

The more perfect SULPHURETTED HYDRO-SULPHURET OF AMMONIA is formed by adding to hydro-sulphuret of ammonia a portion of sulphur, which it dissolves even in the cold. It has a deep yellow colour, and an oily consistence; is decomposed by exposure to the air, the oxygen combining with its hydrogen, and causing a deposition of sulphur.

A combination somewhat analogous, long known to chemists, is that named the Fuming Liquor of Boyle. It is prepared, by exposing to heat in a retort a mixture of sulphur, lime, and muriate of ammonia; a liquor distils over, of a yellow colour, which has a sharp fetid odour, and exhales white vapours. Berthollet submitted it to examination. He collected the product of the distillation in two successive portions. The first he found to be a hydro-sulphuret of ammonia with an excess of ammonia, to which its fuming property appeared to be owing; the white vapours being ammonia, holding a portion of the hydro-sulphuret in solution. The second was not fuming; it was of a deeper colour, and appeared to be a hydro-sulphuret, without an excess of ammonia. On adding to it an equal portion of water of ammonia, it became fuming. Muriatic acid causes a deposition of sulphur from it, and a disengagement of sulphuretted hydrogen gas *. It is probably, therefore, a sulphuretted hydro sulphuret. Accord-

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* Annales de Chimie, t. xxv, p. 244.

ing to Thenard, the smoking takes place in oxygen gas or atmospheric air, but not in nitrogen or hydrogen : the effect probably depends, therefore, on the agency of oxygen.

Ammonia unites with all the acids, forming neutral salts. Its affinities to them appear inferior to those of the other alkalis, as they decompose its salts; but this is probably owing to its volatility; and as a given weight of it saturates larger proportions of the acids, it may, in conformity to Berthollet's views, be regarded as exerting a more energetic action. From the same cause, the inferior concentration of its solution, it acts less strongly on a number of substances ; it combines less intimately with oils, and it does not dissolve the earths : it dissolves, however, even in its liquid state, several of the metallic oxides : and it has a peculiar tendency to form both with them and the earths, in combination with the acids, ternary salts.

The ammoniacal salts seem to retain some distinctive properties from the base. They are in particular all volatile, and when they do not suffer previous decomposition, are in general sublimed at a moderate heat, not exceeding much 3 or 400°. They cannot sustain a red heat, as at that temperature the ammonia itself is decomposed. They are all soluble and crystallizable, and have an acrid taste. They are at once distinguished by the pungent odour they exhale when triturated with a small portion of potash or lime. They throw down an orange-yellow precipitate from muriate of platina. They differ chemically from all other salts in containing no oxygen, but what is derived from their acid ; they are, therefore, quaternary compounds of nitrogen and hydrogen with the radical of the acid, and in general with the whole of its oxygen, and when it is a ternary acid, with the whole also of its hydrogen.

These salts, in conformity to the arrangement I have adopted, are to be considered in connection with the base.

CARBONATE OF AMMONIA.—Ammonia, by combination
with carbonic acid, scarcely has its properties neutralized.
A salt is formed, which, though concrete, is volatile; it
retains the ammoniacal odour and taste, is slightly caus-
tic, and changes the vegetable colours to a green. This
salt may be formed by direct combination, ammonia and
carbonic acid gases instantly combining when presented
to each other. According to Gay-Lussac 100 measures
of carbonic acid gas combine with 200 measures of am-
moniacal gas, and the product is a sub-carbonate.

The usual process, however, to form this compound is
an indirect one. Equal parts of dried chalk, and of mu-
riate of ammonia, are mixed together, and put into an
earthen retort, or an iron pot, to which a capital is adapt-
ed, and which is connected with a large receiver. Heat
is applied, by which a double decomposition is effected.
The lime of the chalk attracts the muriatic acid, and the
ammonia attracts the carbonic acid. The muriate of lime
remains in the vessel, and the carbonate or rather subcar-
bonate of ammonia being volatilized, is condensed on the
sides of the receiver.

There is another process by which it is obtained in so-
lution. Equal parts of muriate of ammonia and of sub-
carbonate of potash are put into a retort with 2 parts of
water, and heat is applied; a double decomposition takes
place, the muriatic acid uniting with the potash, and the
carbonic acid with the ammonia; the carbonate of am-
monia passes over with the aqueous vapour, which, when
condensed, is sufficient to dissolve it.

The compound of carbonic acid and ammonia is also
obtained in the decomposition of animal matter by heat.
If bones be exposed to heat in an iron still, the decom-
position of their gelatin affords a large quantity of the con-
crete salt. This is the salt of hartshorn of the older che-
mists. It is impure and fetid from a portion of empyreu-

matic oil; from this it is partially freed by sublimation from chalk, and completely by sublimation from charcoal.

This salt is very soluble in water; at a mean temperature it requires twice its weight, or, according to some statements, four times its weight, and at 212° less than its own weight is sufficient for its solution. Its saturated solution, on standing for some time, deposites crystals, the figure of which appears to be octohedral. Exposed to a moderate heat, it is volatilized; it is also easily condensed, and its deposition on the sides of the vessel is of a regular dendritic form. It effloresces on exposure to the air, and its odour becomes weaker, from the escape of ammonia, absorption of carbonic acid, and loss of moisture.

According to Bergman, carbonate of ammonia consists of 43 of alkali, 45 of acid, and 12 of water. Kirwan found it to be composed of 24 ammonia, 52 carbonic acid, and 24 of water * ; but, as he remarks, it is known to exist in very different states. Davy observed that the proportions vary in different specimens, from 20 to 50 parts of alkali in 100. The carbonic acid and water are superabundant in it, as the temperature at which it has been formed is low; that formed at 300° contained above 50 of alkali in 100 parts, while that produced at 60° contained only 20 †. These differences are owing to there being in fact two compounds, a subcarbonate and a bi carbonate, the latter containing twice the quantity of carbonic acid which the other contains; and portions of both these are formed, according to the influence of proportions, or temperature : the subcarbonate even absorbs carbonic acid from the air, or allows ammonia to escape, and passes into bi-carbonate. Gay-Lussac states, that in the formation of subcarbonate of ammonia, 100 measures of the acid gas combine with 200 of the alkaline gas; this gives the proportions by weight

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* Transactions of the Irish Academy, vol. vii, p. 267.
† Researches on Nitrous Oxide, p. 76.

of 44 of ammonia and 56 of carbonic acid. The neutral carbonate cannot be formed in this mode; but Berthollet having formed it by passing carbonic acid gas through a solution of the subcarbonate, found it on analysis to consist of 26.66 of ammonia, and 73.34 of carbonic acid. If according to Gay-Lussac's hypothesis it were supposed to be formed of equal volumes of the gases, this would give the proportion by weight of 28.19 of ammonia, and 71.81 of carbonic acid, which does not deviate much from Berthollet's estimate [*]. On Dr Wollaston's scale, the one is composed of 100 of ammonia, with 128 of carbonic acid; the other of 100 with 256.

The bi-carbonate is nearly inodorous; it still changes however the vegetable colours to a green; it forms by spontaneous crystallization from its saturated solution in slender prisms, and appears to be less soluble in water than the subcarbonate.

Carbonate of ammonia, in both states, is decomposed by the fixed alkalis, barytes, strontites and lime, which combine with its acid. Magnesia decomposes it only partially. The acids attract its base, and expel the carbonic acid with effervescence.

NITRATE OF AMMONIA.—This salt is prepared by adding to carbonate of ammonia, nitric acid. It has a cool, bitter taste, is deliquescent, and soluble in two parts of cold water, and in half its weight of boiling water; by the cooling of its solution it crystallizes, the salt obtained being different in its appearance and in the quantity of water it contains, according to the extent of the evaporation and the mode of crystallization. If obtained by slow evaporation, at a temperature not exceeding 70, the crystals are tetrahedral prisms, terminated by tetrahedral pyramids. The solution evaporated at a higher temperature, gives an assemblage of indistinct fibrous crystals, containing less wa-

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[*] Mémoires d'Arcueil, tom. ii, p. 211.

ter of crystallization; and when evaporated fully at 300, it forms a compact mass, in which the quantity of water is still less. In all these, the proportion of the acid to the alkali is the same. The following is a table by Davy of their composition.

Prismatic crystals, acid 69.5 Ammonia 18.4 Water 12.1
Fibrous Salt ———— 72.5 ———— 19.3 ——— 8.2
Compact Salt ———— 74.5 ———— 19.8 ——— 5.7

100 parts of crystallized nitrate of ammonia, by Kirwan's estimate, consist of 23 of alkali, 57 of acid, and 20 of water.

When this salt is exposed to a moderate heat, it undergoes the watery fusion. The water of crystallization is expelled, and part of the salt is volatilized with it. The greater part, however, remains as a dry mass; if the heat is increased, this is decomposed; and if raised to ignition, is decomposed with detonation. This arises from the peculiar composition of this salt: the nitric acid and ammonia which form it being both decomposed by the heat; the oxygen of the one combines with the hydrogen of the other, and form aqueous vapour, which is suddenly disengaged with a large quantity of nitrogen gas.

Davy in his researches on nitrous oxide, determined the circumstances of this decomposition. He found that the detonation is produced only above 600°, and along with nitrogen and watery vapour, nitric oxide and nitrous acid are disengaged. At lower temperatures, it decomposes more slowly, water and nitrous oxide being the products. The different varieties of the salt suffer the same change at different temperatures. The compact salt between 275 and 300 sublimes slowly, without decomposition, or without becoming fluid; at 320 it becomes fluid, sublimes, and also decomposes; between 340 and 480 it decomposes rapidly. The prismatic or fibrous salt becomes fluid at temperatures below 300, and between 360 and 400 sublimes without decomposition, nor does it decompose but at tem-

peratures above 450 *.   These decompositions give rise to
the combination of oxygen and hydrogen, and oxygen and
nitrogen, in those proportions which form water and ni-
trous oxide ; and it is from the decomposition of this salt
that nitrous oxide is best procured.

SULPHATE OF AMMONIA.—This salt crystallizes in slen-
der six-sided prisms acuminated by six planes.   It is solu-
ble in about two parts of water at 60°, and in an equal
weight at 212°.   Exposed to heat, it melts, and is decom-
posed, part of the ammonia being exhaled.   At ignition, it
is decomposed by the re action of its ultimate elements, the
hydrogen of the ammonia attracting part of the oxygen
of the acid, and sulphurous acid and nitrogen gases being
disengaged.   It deflagrates weakly when heated with nitre.
Like the other sulphates it is partially decomposed by ni-
tric and muriatic acids.   The fixed alkalis, lime, barytes
and strontites, attract its acid, and with the assistance of
heat displace the ammonia.   According to Kirwan, it
consists of 54.66 of acid, 14.24 of ammonia, and 31.1 of
water.   It has been said to have been found in the neigh-
bourhood of volcanoes.   The saline matter extracted from
soot by maceration in water consists partly of it ; it must
therefore be formed in the combustion of coal.

This salt appears to enter easily into combination with
other sulphates, and thus to form triple salts, such as sul-
phate of potash and ammonia, sulphate of magnesia and
ammonia, &c.   The composition of several of these has
been assigned by Link †.

SULPHITE OF AMMONIA is very soluble in water, re-
quiring less than its weight of boiling water for its solution.
This solution crystallizes on cooling ; its crystals are six-
sided prisms acuminated with six planes, white and trans-
parent.   Its taste is cool and sulphureous.   Exposed to

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* Researches, p. 87.
† Annals of Philosophy, vol. ii, p. 296.

air it attracts humidity, and passes into a sulphate; it is fused and volatilized by heat without decomposition. It contains 29 of ammonia, 60 of acid, and 11 of water.

PHOSPHATE OF AMMONIA exists in the urine of carnivorous animals, in considerable quantity, united with phosphate of soda, forming a triple salt, known to the older chemists by the name of Microcosmic, or fusible salt of urine. To obtain it pure, it must be formed by the combination of its principles. It is soluble in 4 parts of water at 60°; it crystallizes readily; the form of its crystals being a four-sided prism acuminated with four planes By exposure to heat, it is first fused into a transparent glass, and then decomposed, part of its ammonia being expelled. When mixed with charcoal, and exposed to heat, its acid is easily decomposed. It is decomposed by the other two alkalis, by barytes, lime, and even by magnesia. Like phosphate of soda, it may be used with advantage in analyses by the blow-pipe.

PHOSPHATE OF SODA AND AMMONIA.—This triple salt, existing in several of the animal fluids, engaged much the attention of chemists. From the researches of Fourcroy, it appears to be variable in the proportion of its elements, the quantity of phosphate of ammonia diminishing as it is repeatedly crystallized. One variety obtained by a first solution and crystallization, he found to consist of 32 parts of acid, 24 of soda, 19 of ammonia, and 25 of water. It has generally an excess of alkali, effloresces in the air, is abundantly soluble in water, and very fusible, being also decomposed when fused.

PHOSPHITE OF AMMONIA has a strong penetrating taste. Its solution affords delicate acicular crystals. Exposed to the blow-pipe it intumesces and is decomposed, phosphuretted hydrogen gas being disengaged, which burns vividly in the air, with the white circular smoke peculiar to the combustion of that substance. It is likewise decomposed by distillation in a retort, the ammonia being expelled

partly in a liquid state, and partly in that of gas, holding
a small portion of phosphorus in solution, phosphoric acid
being the residuum. It is decomposed by the other al-
kalis, by lime and barytes. According to Vauquelin, it
consists of 51 of ammonia, 26 of acid, and 23 of water.

HYPO-PHOSPHITE OF AMMONIA is a salt described by
Dulong as being very soluble in water, and also soluble in
alkohol.

BORATE OF AMMONIA.—This salt is little known, and
can scarcely indeed be obtained in a solid state. If am-
monia is saturated with boracic acid, on evaporating the
solution, the greater part of the ammonia is disengaged.
By slow evaporation, however, prismatic crystals have
been obtained of a sharp taste, having an excess of alkali
so as to change the vegetable colours to a green : by heat
they are decomposed, the ammonia being expelled.

MURIATE OF AMMONIA.—This salt is formed when its
constituent gases are presented to each other. According
to Priestley about equal measures are requisite to neutra-
lization. Gay-Lussac and Thenard have stated that they
combine in exactly equal measures, and that the salt is
perfectly neutral : they infer the composition by weight,
from their estimate of the specific gravity of muriatic acid
gas, to be 38.35 of ammonia, and 61.65 of acid ; the lat-
ter containing, however, one-fourth of its weight of water.
The proportions, including this water as existing in the
composition of the gas, are inferred by Berzelius to be 33
of ammonia and 67 of acid ; and supposing the latter to
retain in combination $\frac{1}{4}$ of water, the proportions will be 33
of ammonia, 50.3 of real acid, and 16.7 of water. Kir-
wan states the composition of sublimed muriate of ammonia
at 28 of ammonia, 42.75 of acid, and 29.25 of water.

This salt is the Sal-Ammoniac of commerce. It is
found as a product of volcanoes and pseudo-volcanoes, but
in small quantity ; and for use, it is always prepared by
art. A manufacture of it had been established in Egypt

from time immemorial.   It is procured, according to the
account that has been given, by sublimation from the soot
of fuel *.   Large quantities of it have been prepared in
Europe for a number of years past, so that the Egyptian
sal-ammoniac is no longer imported.

The process is different in different manufactories. The
soot of coal by maceration in water affords a quantity of
sulphate of ammonia   this is mixed with muriate of soda;
the mixture, being dried, is exposed to a strong heat: a
double decomposition takes place; the sulphuric acid of
the sulphate of ammonia unites with the soda of the mu-
riate of soda, while the muriatic acid combines with the
ammonia: the muriate of ammonia is sublimed, the sul-
phate of soda remains at the bottom of the vessel. Or what
is a preferable mode, the mutual decomposition is effected
in the humid way by boiling the solution of the salts, the
sulphate of soda is separated by crystallization, and the
muriate of ammonia being obtained by evaporation is sub-
limed.   Sulphate of ammonia is also sometimes procured
by saturating the impure ammonia, obtained by distillation
from animal substances, with sulphuric acid, obtaining the
salt by evaporation, and decomposing it by muriate of so-
da, in the manner above described.   Another process is to
disengage the muriatic acid from muriate of soda by sul-
phuric acid in the usual manner, combine it with the im-
pure ammonia, and afterwards sublime the compound salt;
or to form the salt by presenting muriatic acid to ammonia
evolved in its nascent state from the decomposition of dif-
ferent kinds of animal matter by heat.

From the manner in which this salt is prepared, by sub-
limation in globular vessels, it is in the form of semi-sphe-
rical cakes, having a polished surface, and a texture some-
what ductile, of a greyish white colour.   It is capable of
crystallization by solution in boiling water and cooling, its

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* Philosophical Transactions, vol. li, p. 504.

crystals being tetrahedral prisms acuminated by 4 planes. They suffer little or no alteration by exposure to the air, at least if they deliquesce it is in an inconsiderable degree, and only in a humid atmosphere. The taste of this salt is acrid and cool. It requires about $3\frac{1}{2}$ of water, at 60°, to dissolve it. Boiling water dissolves nearly its own weight of it. Exposed to heat, it is volatilized, even before it is melted, and with little or no decomposition. It is decomposed by the sulphuric and nitric acids, which combine with its alkali, and by potash, soda, barytes, and lime, which unite with its acid. It is also decomposed by the carbonates of potash, soda, and lime, by which carbonate of ammonia is obtained. It is used in several arts. In soldering, it cleans the surface of the metals to be united, and prevents their oxidation ; in dyeing, it renders several colours brighter ; and it is often used in pharmacy and in a number of chemical processes.

HYPER-OXYMURIATE OF AMMONIA.—The formation of this salt might be thought impracticable, as ammonia is decomposed when presented to oxymuriatic gas. Though it cannot be produced by the usual process, Mr Chenevix succeeded in obtaining it, by pouring a solution of carbonate of ammonia into the solution of an earthy hyper-oxymuriate ; a double decomposition ensued, and hyper-oxymuriate of ammonia was formed. He describes it as very soluble in water and in alkohol : It is decomposed at a low temperature, giving out a quantity of gas, and a smell of hyper-oxymuriatic acid. Vauquelin has since examined this salt more minutely : it crystallizes, he remarks, in fine needles, and appears to be volatile, as there is a considerable loss in evaporating its solution ; its taste is extremely sharp ; it detonates when placed on a hot body, with a red flame ; decomposed by heat it gives out chlorine gas, with nitrogen, and a little nitrous oxide, muriate of ammonia with muriatic acid remaining [*].

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[*] Annales de Chimie, t. xcv. p. 98.

FLUATE OF AMMONIA has a very sharp taste; it is extremely susceptible of decomposition, its solution during evaporation merely becoming acid; on continuing the heat it volatilizes entirely in very dense white vapours.

SILICEO-FLUATE OF AMMONIA appears to be formed as a definite compound when the two gases are presented to each other; the combination taking place, as Gay-Lussac found, in the proportion exactly of one volume of the siliceo-fluoric acid gas, and two volumes of the ammoniacal gas. It consists, therefore, of 24.5 of ammonia and 75.5 of acid by weight. It condenses into a solid deposite, which may be volatilized unchanged by a moderate heat. It is decomposed by water, and part of the siliceous earth is separated; a portion remains in combination, and a similar result is obtained when ammonia is added to the liquid siliceo-fluoric acid; the solution has a pungent acidulous taste; is very soluble; by slow evaporation it is obtained in small transparent brilliant crystals, tetraedral prisms, and is sublimed undecomposed by heat. This salt consists, according to Mr J. Davy, of 28.34 of ammonia and 71.66 of acid. When saturated by ammonia, the whole of the silica, he finds, is separated *.

FLUO-BORATE OF AMMONIA is produced when fluo-boric acid gas and ammoniacal gases are presented to each other. They unite, according to J. Davy, in the proportion of equal volumes, and also in the proportion of one volume of the acid with two of the ammonia, and in that of one of the former with three of the latter. There are therefore three definite compounds: the first proportion gives a solid product which appears to be the neutral compound; the other two are liquid: they are volatilized by a gentle heat, and when left exposed to the atmosphere, allow the excess of ammonia to escape.

HYDRIODATE OF AMMONIA is formed from the combi-

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* Philosophical Transactions, 1812.

nation of equal volumes of ammoniacal gas and hydriodic acid gas. It is nearly as volatile as muriate of ammonia, and is more soluble and deliquescent; it crystallizes in cubes. When heated in close vessels it suffers little decomposition, but sublimed in contact with the air, it suffers greater decomposition, and becomes coloured from the production of iodine.

OXIODATE OF AMMONIA, formed by saturating oxiodic acid with ammonia, is obtained in small granular crystals; it detonates on burning fuel, giving out a purple light, and vapours of iodine; it is decomposed by heat, and gives iodine, oxygen, and nitrogen with water. Gay-Lussac calculates that it is a compound of 100 of acid with 10.94 of ammonia.

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CHAP. II.

OF POTASH AND ITS BASE.

THIS alkali has been long known to chemists under various appellations. Being obtained from the burning of vegetables, it was named Fixed Vegetable Alkali: as it is the basis of the saline matter known in commerce by the name of Potashes, it was termed Potasse by the authors of the new nomenclature, a name which has been received into the English language, though that of Potash has been usually preferred. Dr Black gave it, from Pliny, the name of Lixiva; Kirwan imposed that of Tartarin; and by the London College it was named Kali. The term Potassa has been received as the Latin appellation, and would be preferable also in our language as distinct from the potash of commerce, and analogous in termination to

the names of the other alkalis, but that of potash appears
to be established.

From the analogy of potash with ammonia, it had often
been supposed to be a compound, and conjectures had
been advanced with regard to its composition.   Chaptal
had supposed it to be a compound of nitrogen and lime.
Guyton and Desormes, from some experiments, inferred
that it is a compound of lime with hydrogen.   These,
Darracq found insufficient to establish the conclusion that
had been drawn from them *.   Nothing, therefore, was
truly known with regard to the nature of this alkali ; and
the discovery of its composition by Davy, when it was
accomplished, shewed how imperfect the analogies were
from which these conjectures had been drawn.   The dis-
covery must be regarded as one of the most important in
chemistry, as having introduced to the knowledge of the
chemist a class of substances altogether peculiar, and ha-
ving little analogy with those before known, and having es-
tablished views of extensive influence in the relations of the
science.

He was led to institute experiments with a view to de-
compose the fixed alkalis, by the knowledge of the power-
ful energy of galvanic electricity in subverting chemical
combination, and causing the evolution of the elements of
compounds in a separate state.   He first exposed the al-
kali dissolved in water to the action of the galvanic bat-
tery, but the water alone was decomposed. Potash in fu-
sion was then placed in the galvanic circuit ; a vivid light,
and appearances of the production of combustible matter
were observed ; on submitting the solid alkali, rendered a
conductor of electricity by being very slightly moistened,
to the galvanic action, these appearances were better mark-

* Mémoires de l'Institut National, tom. iii, p. 322.
  Philosophical Magazine, vol. xi. p. 344.

ed ; and it was this method that succeeded in effecting the decomposition. A small piece of pure potash, exposed for a few seconds to the atmosphere, was placed upon an insulated disc of platina, connected with the negative side of the battery, in a state of intense activity, and a platina wire, communicating with the positive side, was brought in contact with the upper surface of the alkali. A vivid action was soon observed to take place : the potash began to fuse ; an effervescence took place at the upper surface ; at the lower, or negative surface, small globules, having high metallic lustre, and similar to quicksilver, appeared, some of which burnt with explosion and bright flame as soon as they were formed, and others remained, and were tarnished, and finally covered by a white film. These globules, numerous experiments soon shewed to be a peculiar substance, the base of potash *.

In conformity to the usual law of galvanic decomposition, it was to be inferred that the gas disengaged at the positive wire was oxygen gas. Mr Davy accordingly found it to be so : unless an excess of water was present, there was no liberation of gas at the negative surface, nothing being produced there but the inflammable globules.

From these results, he inferred that potash is a compound of a substance, highly inflammable, and having metallic lustre, with oxygen. To this substance he gave the name of Potassium, and by synthetic experiments on it established the same conclusion.

He found its metallic lustre to be destroyed in the atmosphere, and a white crust formed upon it, which was pure potash. This soon dissolved, by attracting humidity from the air; and a new quantity was formed, until the whole disappeared, and formed an alkaline solution. When the globules were placed in tubes containing atmospheric

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* Philosophical Transactions, 1808.

air or oxygen gas, an absorption of oxygen took place, and a crust of alkali was formed. When they were strongly heated in oxygen gas, combustion with a brilliant white flame was produced, and they were converted into a white solid mass, which was found to be potash : oxygen was absorbed, and nothing emitted which affected the purity of the residual air. From the results of this experiment, he inferred that potash consists of 86.1 of potassium and 13.9 of oxygen. From the results obtained by the action of water, the proportions appeared to be 84 and 16.

The production of potassium from potash by galvanism is considerably facilitated by another mode of conducting the experiment, which seems first to have been employed by Ritter *. It consists in placing potash in contact with the positive side of a galvanic battery, putting a globule of quicksilver upon it, and touching this with a wire from the negative side. The potassium as it is produced combines with the quicksilver, enlarges its volume, and renders it solid ; and the quicksilver may afterwards be separated by distillation.

By any modification, however, of galvanic action, potassium can be procured in a very minute quantity only, even with the most powerful battery. An important discovery, therefore, by Gay-Lussac and Thenard, was that of a process by which it can be procured in larger quantity, in consequence of which, its properties and chemical relations have been determined with more precision. Their process consists in subjecting potash to the action of iron at a high temperature. A gun-barrel is bent, so that about one-third of its length shall be included in the curvature, the unbent parts shall have a moderate inclination, and the straight part at the thicker end of the barrel shall be longer than at the other. The curved part is coated with a lute of clay and sand ; and within are placed in it clean iron

* Annales de Chimie, t. lxvi, p. 92.

turnings; it is put across a furnace, so that the curvature
occupies the body of the furnace, and the extremities are
without; in the upper end of the gun-barrel are placed
three or four ounces of potash, which has been previously
exposed to a red heat; to this extremity is adapted a glass
tube bent at a right angle, so that the open end of it can
be immersed in quicksilver; to the other end of the gun-
barrel an iron tube is adapted, with which is connected a
glass tube, bent so, that it may also be immersed in water
or quicksilver.   The fire is raised in the furnace to a very
bright red, or white heat, the straight part of the tube be-
ing kept cool, by wet linen, that the potash in it may not
liquefy; when the heat is raised sufficiently high, this part
of the tube is heated by a choffer of charcoal, so that the
potash melts slowly; as it melts, it reaches the hotter part,
is converted into vapour, and passing over the iron turn-
ings is converted into potassium.   This is accompanied
with a copious disengagement of hydrogen gas from the
decomposition of the combined water of the potash; this
escapes by the bent glass tubes.   The potassium is volati-
lized, and condenses at the extremity of the tube, and in
the iron tube connected with it.   When the gas ceases to
be disengaged, the gun-barrel is withdrawn, the openings
of the tubes being closed with lute, and it is allowed to cool;
the potassium is condensed in brilliant plates, at the short
extremity with which the iron tube is connected, and in
the tube itself; the barrel when cold is cut through at this
place.   The quantity obtained is from four to six drachms:
but much of the potash remains undecomposed, combined
with oxide of iron *.

This operation is attended with considerable difficulty.
Gay-Lussac and Thenard have pointed out the circum-
stances most essential to its success.   The potash prepar-

* Mémoires d'Arcueil, tom. ii, p. 299.   Recherches Physico-
Chimiques, tom. i, p. 74.

ed from the potash of commerce usually contains a portion of soda, which affords sodium, and this combines with the potassium; it ought therefore to be prepared from the deflagration of nitre with tartar; it ought to be as free as possible from water; the iron turnings must be quite clean and bright; the iron-barrel must be clean; and much care is requisite in preparing and applying the lute, as if this does not adhere closely, the iron oxidates and fuses during the operation. The potash ought to be melted slowly, as if it pass too rapidly over the iron, it reduces the temperature below what is necessary to obtain the result. Other forms of apparatus somewhat varied, more economical or more simple, have since been introduced [*]. Mr Chilton found, that a gun-barrel may be employed without any curvature, the potash from its volatility being converted into vapour, and passing over the iron. And Mr Tennant greatly simplified and improved the apparatus,—employing a gun-barrel, into which the dry potash and iron-filings were put; into the open end of the gun-barrel a narrower piece is inserted, open at the extremity opposite the closed end of the gun-barrel, so that the vapour of the potassium enters into it and is condensed; and at the open end of the gun-barrel, including this piece, is adapted a close cap or wide tube, with a curved glass tube passing from it, to allow of the escape of the permanent gas [†].

Regarding potash as a compound of potassium and oxygen, it must be supposed that in this experiment its oxygen is abstracted by the iron from the affinity of that metal to this element, aided by the temperature. The hydrogen disengaged is derived from the decomposition of the water contained in the potash; and this hydrogen, by its affinity to the potassium, and its power of dissolving it

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[*] Philosophical Magazine, vol. xxxv. Bruce's Mineralogical Journal, vol. i.

[†] Philosophical Transactions, 1814, p. 578.

at an elevated temperature, favours probably its produc-
tion.

It appears that similar results can be obtained, though
less perfectly, by the medium of charcoal. Dr Woodhouse
found, that a mixture of pearl-ash with soot, calcined by
an intense heat in a covered crucible, caught fire when
cold on the affusion of water; the experiment was repeat-
ed with charcoal with the same result; and the inflamma-
tion probably arose from the action of the base of the al-
kali on the water *. The substance named Homberg's
Pyrophorus, which inflames spontaneously on exposure to
the air, and in the preparation of which the presence of
potash is known to be indispensable, appears also to con-
tain potassium, and to owe its inflammability to it.

A process has even been given by Curaudau for obtain-
ing potassium by the agency of charcoal. It consists in
calcining, in an iron or earthen tube, a mixture of an alka-
line carbonate, either potash or soda, with charcoal and
linseed oil; the fire is raised until a blue light is perceived
in the interior of the vessel : to this a vapour succeeds,
which is the metallic base of the alkali. It may be collect-
ed, by introducing a clean iron rod, on which it condenses,
withdrawing the rod before it becomes too hot, and plung-
ing it in oil of turpentine, so as to detach the metallic
crust : a quantity may thus be procured †. Bucholz suc-
ceeded in obtaining potassium by this process ‡. Gay-
Lussac and Thenard observe that it succeeds imperfectly,
unless iron is added, or an iron vessel employed.

Gay-Lussac and Thenard proposed a theory of the pro-
duction of potassium, different from that advanced by Mr
Davy. Instead of regarding potash as a compound of a
metallic base with oxygen, they supposed it to be a simple

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* Nicholson's Journal, vol. xxi, p. 290.
† Ibid. vol. xxiv. p. 37.
‡ Ibid. vol. xxix, p. 186.

body, and the potassium a compound of it with hydrogen. In its production they supposed the water present to be decomposed, and its hydrogen to combine with the potash and form the potassium. And in the reproduction of potash from this, they supposed the oxygen consumed to combine with this hydrogen, form water, and leave the potash in an insulated state. On this hypothesis the peculiar levity of potassium seemed to be better explained than on the other, since it might be ascribed to the presence of the hydrogen.

When it was proposed, Mr Davy supposed it to be refuted by the facts, that potassium may be produced from dry potash, and that by oxygenation it may be converted into potash without any sensible production of water. But these are inconclusive, since even ignited potash contains a large portion of combined water, which may afford, on the hypothesis of Gay-Lussac and Thenard, the quantity of hydrogen necessary to the constitution of potassium; and in the reproduction of potash may retain the water formed.

The mode of investigation by which the truth of the hypothesis is to be determined, is, to ascertain the alkaline strength of the potash formed by the oxygenation of potassium, compared with that of common ignited potash. If potassium be potash with the hydrogen of the water, which ignited potash contains, it ought, when it is again combined with oxygen, to reproduce the alkali with the same quantity of water combined with it; while, if potassium be the base of potash, it ought, in combining with oxygen, to form it free from water, and therefore superior to common potash in alkaline strength.

To determine this, Mr Davy converted potassium into muriate of potash by the action of muriatic acid gas, and inferred, from the results of the experiment, that by the quantity of potash produced by the oxygenation of the potassium, a quantity of salt was formed, which would have required a much larger portion of fused potash, according

to Berthollet's estimate of the composition of this salt; the former, therefore, had not contained the water contained in the latter. The experiment has been also made by Gay-Lussac and Thenard in a more direct manner. Potassium, when it has absorbed a large quantity of oxygen, forms an oxide containing more oxygen than potash; when they introduced to this oxide carbonic acid, oxygen was expelled and subcarbonate of potash formed; when sulphurous acid was introduced, sulphite of potash was produced; but in neither case was there the slightest appearance of humidity; and it cannot be supposed but that this would have been apparent, had the potassium from which these oxides were formed contained the hydrogen of the water, which fused potash contains [*].

These facts are conclusive against the hypothesis, that potassium is potash combined with hydrogen; or at least with that quantity of hydrogen which the water existing in fused potash contains: these chemists accordingly relinquished it, and adopted the opinion, that potash is a metallic oxide, and that potassium is its base.

Still this is not strictly established: it presents some difficulties, and a different view may be proposed of the nature and relation of these substances.

While ignited potash was supposed to be the real alkali, the phenomena observed in submitting it to galvanic action, as stated by Davy, corresponded with the theory which he gave of the experiment; for if oxygen is disengaged at the positive side, and nothing appears at the negative side but the globules of potassium, the potash may be considered as resolved into these two elements. But since potash contains combined water, a considerable evolution of hydrogen gas ought to take place at the negative pole from its decomposition; and since it does not appear, it must be inferred that it enters into the composition of the

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[*] Recherches Physico-Chimiques, tom. ii, p. 250.

matter which collects there ; that it must therefore be an ingredient in potassium.

This appears to lead to the hypothesis of Gay-Lussac and Thenard, which, however, from the facts already stated, cannot be maintained. I proposed a different view of this subject. Potash may be regarded as a compound of oxygen with a metallic base, and as being decomposed when submitted to galvanic action. The water it contains must equally be decomposed, and the oxygen of both will be disengaged at the positive pole. The base of the alkali and the hydrogen of the water must be attracted to the negative pole ; and as the hydrogen is not disengaged, or at least not in the quantity to be expected from the portion of water the potash contains, it may be inferred that they combine, and that the potassium is the product of this combination. When potash is decomposed by iron, it must be concluded, in conformity to this view, that the iron attracts the oxygen of the alkali and of the water, and the metallic base of the former combines with a portion of the hydrogen of the latter. Potassium, therefore, according to this view, is a compound of the metal of potash with a proportion of hydrogen ; and to the presence of this hydrogen may be ascribed its peculiar qualities, and, in particular, its great levity, which distinguish it so remarkably from the common metals. Hydrogen, it is to be remarked, in confirmation of this opinion, has an affinity to potassium, and combines with it. They combine even in different proportions, one compound being gaseous, another existing in the solid form. It is obvious, that the real metallic base may combine with a still smaller proportion of hydrogen ; and as the simple inflammables, carbon, sulphur, and phosphorus, form compounds with metals, in many of which the lustre, opacity, density, and other characteristic metallic properties are not impaired, the same result may be established in the combi-

nation of hydrogen, at least when it is within a certain proportion, and, while it admits of the general metallic qualities remaining, may give rise to some of the more anomalous properties which distinguish potassium.

The mode by which this opinion may be brought to the test of experiment, is evidently to determine whether the alkali formed by the oxygenation of potassium is equal in the power of neutralizing acidity to real potash, that is, to potash abstracted from water, such as it exists in saline compounds, and which consists of potassium and oxygen alone ; for if potassium contain a portion of hydrogen, the alkali it affords must yield combined water, and must be so far inferior in alkaline strength to the quantity of real potash formed from the same quantity of potassium. I refer to the experimental investigation which I undertook of this subject *, stating merely the general result I obtained,—that the potash formed by the oxygenation of potassium, though much superior in alkaline strength to fused potash, is not equal to real potash,—a result which appears to establish the conclusion, that potassium contains hydrogen combined with the metallic base.

It remains to state the properties of Potassium, previous to the history of the alkali itself.

POTASSIUM has the obvious properties of a metal, lustre and opacity : At common temperatures it is solid, and has a dull white colour nearly resembling silver ; it tarnishes quickly, on exposure to the air, and has the colour of lead. It is soft, and can be easily extended or cut by a knife. This is its consistence at 50° of Fahrenheit, but it is remarkable for the changes it suffers within a slight range of temperature ; at 60° it becomes imperfectly fluid ; at 70° it is more liquid and mobile; and at 100° it is so much so, that different globules can be easily run into one.   These

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* Nicholson's Journal, vol. xxviii, p. 241. 359.

are the results found by Mr Davy. Its fusibility, however, is not so great. According to Gay-Lussac and Thenard, the proper fusing point of potassium is 136°. At 32° it becomes hard and brittle, displaying when broken, facets indicating a crystalline texture. Though fusible, it is not very volatile, but requires a temperature approaching to a red heat to convert it into vapour. It is a perfect conductor of electricity and of heat.

In these properties it has the closest resemblance to metals ; and it might be expected also to resemble them in the characteristic property of density. It is however lighter than water, or even alkohol or ether. Davy found that it did not sink in naphtha, the specific gravity of which was .770. Its specific gravity he estimates, compared with that of water, as 0.6 to 1 at 62° of Fahrenheit. According to Gay-Lussac and Thenard, it is considerably greater, being at 59° 0.865,—an estimate which appears to be just, at least with regard to the potassium obtained by the medium of iron, as it sinks in naphtha.

The chemical relations of this substance are not less singular than its physical properties.

It combines with oxygen slowly, and without flame, at all temperatures below that of its volatilization ; and so liable is it to oxygenation, that it is difficult to preserve it unchanged : the best mode is to keep it in naphtha. At the temperature at which it volatilizes, it burns in atmospheric air ; and in oxygen gas the combustion is very vivid. The metallic globules, Mr Davy stated, are converted into a white and solid mass, which is potash. But, besides this product, he farther found, that when potassium is heated slowly in a quantity of oxygen gas not sufficient for its complete conversion into potash, and at a temperature inadequate to its inflammation, as 400° of Fahrenheit, a solid is formed of a greyish colour, which he supposed to consist partly of potash, and partly of potassium, in a lower degree of oxygenation, and which becomes potash on

being exposed to water, or by being again heated in fresh
quantities of air. The same substance, he remarked, may
be formed by fusing dry potash with potassium ; and it is
often formed in the galvanic decomposition of potash when
the action is intense. The quantity of oxygen absorbed
in the perfect combustion of potassium he found to a-
mount to about 18 by 100 parts. And the quantity com-
municated to it by water, in converting it into potash, was
nearly the same as estimated from the quantity of hydro-
gen gas disengaged [*]. These experiments were made on
small quantities of potassium ; but at a later period, the
results differed very little when considerable portions were
operated on [+].

The oxygenation of potassium was afterwards investi-
gated by Gay-Lussac and Thenard, and very different re-
sults established. The product of the combustion of po-
tassium, whether in atmospheric air or in oxygen gas, is
not potash, but an oxide at a much higher degree of oxi-
dation : in the formation of it, therefore, much more oxy-
gen is consumed than when potash is the product. And
there is a third oxide in a lower degree, and probably at
the minimum of oxidation [‡].

The first of these oxides contains about three times the
quantity of oxygen which potash contains ; it is of a yellow
colour when pure, but if prepared on platina, has a brown
colour from the intermixture of oxide of platina ; it is fu-
sible by heat, but less so than common potash, and it crys-
tallizes in thin plates on cooling. When brought into con-
tact with water, there is an immediate effervescence with
much heat, oxygen gas is disengaged, and potash is form-
ed, which the water dissolves. Its action is energetic on
inflammable and metallic bodies ; it oxidates them, passing

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[*] Philosophical Transactions 1808.
[+] Ibid. 1810.
[‡] Recherches Physico-Chimiques, t. i, p. 125.

in general to the state of potash, and this is in many cases attended with inflammation. These chemists found, that potash exposed to a red heat absorbs oxygen, and passes more or less perfectly into this oxide at the maximum of oxidation.

That degree of oxidation of potassium, which forms potash, appears to be established almost exclusively by the agency of water. When the potassium is dropt into water potash is formed, as it is also under exposure to a humid atmosphere; and it is equally formed by the action of water on either of the other oxides, oxygen being expelled from the oxide at the maximum, and hydrogen being disengaged by the oxide at the minimum. From the quantity of hydrogen gas evolved from the decomposition of water by potassium, Gay-Lussac and Thenard have inferred, that 100 parts of it, in forming potash, combine with 19.9 of oxygen, so that 100 of potash consist of 83.37 of potassium and 16.63 of oxygen.

The third oxide is formed by inclosing potassium in a vessel of small size, full of air, and closed with linen, the air affording oxygen, and the linen transmitting a little hygrometric water, which favours the oxidation through the whole mass. This oxide is dull, brittle, very inflammable and decomposes water, attracting its oxygen, and disengaging hydrogen. It is not improbable that it may consist of potash with a portion of potassium intermixed.

The action of water on potassium is very energetic; hydrogen gas is disengaged, and the potassium becoming potash, soon disappears: this is attended with considerable heat, but with no inflammation if the air be excluded: if it is dropt on water under exposure to the air, the potassium kindles at the surface, probably from the heat produced aiding its attraction to the oxygen of the air, and partly from the nascent hydrogen dissolving a portion of it, and presenting it to the air: there is accordingly often a disengagement of a white ring of smoke, which extends

as it rises in the atmosphere,—an appearance which must be owing to the inflammation of hydrogen holding potassium dissolved. When placed on ice, it instantly burns with a bright flame, melting the ice.

Potassium, thrown into solutions of the mineral acids, inflames and burns on the surface, and the compound of potash with the acid employed is formed. It also burns in the acid gases: in some of them, as in nitrous acid vapour, and oxymuriatic acid gas, with inflammation, even at a common temperature; in others, as muriatic acid gas, without inflammation; but if the temperature be raised it burns, and it burns likewise when heated in carbonic acid gas, sulphurous acid gas, and fluoric acid gas. The potassium in all these cases is oxidated, by decomposing either the acid or the water it contains.

When heated in nitric and nitrous oxide gases it inflames: it abstracts oxygen from a number of metallic oxides, and from many of the neutral and metallic salts. By the same kind of action it changes the constitution of the alkalis and alkaline earths. If it be heated with fused potash, a large quantity of hydrogen is disengaged; and products are obtained, which appear to be oxides at a lower degree of oxidation than potash, or mixtures of these with potash. With soda the results are similar. Mixtures of the earths with potassium also afford, according to Gay-Lussac's experiments, portions of hydrogen; and dark-coloured products are obtained, which excite effervescence with water.

Its action on ammonia is more peculiar. When it is melted in the ammoniacal gas, it is changed into a substance of an olive green colour, very fusible, the ammonia almost entirely disappears, and is replaced by a volume of hydrogen, which, according to Gay-Lussac and Thenard, is precisely equal to that which the quantity of potassium employed would give from its action on water. Mr Davy repeated their experiments, and observed the formation of

the olive-coloured matter and the evolution of hydrogen; the proportion of ammonia absorbed he found to be variable, according as the gas was more or less free from moisture. The olive-coloured product is opaque, unless in thin films, and has no metallic lustre; its fracture presents crystalline facets; it is heavier than water; it melts at a heat a little above 212°; it then gives out gas, which consists of ammonia, and hydrogen and nitrogen in the proportions which form ammonia, and becomes solid, preserving its green colour: the ammonia evolved, either in its insulated state, or in that of its elements, amounts to about three-fifths of the quantity which had been absorbed, and the remaining two-fifths is obtained when a few drops of water are added to the residual matter: if instead of adding water, a very strong heat be applied, nitrogen gas is evolved. Heated to ignition in contact with the air it burns; and when fused in oxygen gas, its combustion is vivid, nitrogen is given out, and potash is formed; water acts on it with violence, considerable heat is produced, and sometimes inflammation; potash is formed, and ammonia evolved equal to what had been absorbed. The mineral acids decompose it, and salts are formed of the acid and potash.

The determination of the nature of this substance afforded a question of some interest, from being connected with the theories with regard to the nature of potassium. Gay-Lussac and Thenard considering potassium as a compound of potash and hydrogen, supposed it to be a compound of potash and ammonia; the hydrogen disengaged in its production being the portion contained in the potassium. On the opposite hypothesis, it must be supposed that the ammonia is in part decomposed by the potassium, and affords this hydrogen disengaged; and the olive-coloured product is, in conformity to this, a compound of potassium with the remaining ammonia, and the nitrogen of the portion decomposed. There is, however,

much difficulty in giving the true theory of the action of potassium on ammonia ; the experiments being so refined, and exposed to so many sources of fallacy.

Potassium combines with the simple inflammables. With hydrogen it appears to unite in different proportions. When heated in hydrogen gas, at a degree below its point of vaporization, it diminishes in volume, and the gas explodes with the production of alkaline fumes, when it is presented to atmospheric air : a portion of the potassium, therefore, has been dissolved ; by cooling, a great part of this appears to be deposited, as the gas loses the property of detonating at natural temperatures. According to Gay-Lussac and Thenard, a combination of hydrogen and potassium in the solid form may also be formed. It is obtained by heating potassium in hydrogen gas over mercury, at a particular temperature,—that excited by the flame of spirit of wine ; the potassium melts, and the quicksilver rises rapidly, proving the absorption of the hydrogen ; if the heat be raised a little too high it again falls, from the decomposition of the hydruret and the evolution of its gas. This solid hydruret of potassium they describe as of a grey colour, without metallic appearance, and infusible ; it does not inflame either in the air or in oxygen gas at ordinary temperatures, but at an elevated temperature burns vividly ; with water it gives out hydrogen ; put in contact with air and water it burns like potassium. By heat it is decomposed, its hydrogen is expelled, and the potassium is reproduced ; it is also decomposed by quicksilver, an amalgam being formed, and hydrogen disengaged. Gay-Lussac and Thenard add, that they have reason to believe, that a hydruret of potassium with a still smaller proportion of hydrogen exists, and which is possessed of metallic lustre. Sir H. Davy was unable, in repeating these experiments, to form the solid compound of potassium and hydrogen ; but these chemists affirm, that they have obtained it in nu-

merous repetitions of their experiment, so as to leave no room to doubt of its existence *.

When potassium is brought into contact with phosphorus under exposure to air, both bodies become fluid, burn, and phosphate of potash is formed. When the experiment is made under naphtha, they unite and form a compound less fusible than either of its ingredients. It is similar in appearance to the compounds of metals with phosphorus, is of the colour of lead, and has a lustre similar to that of polished lead. According to the French chemists, it has no metallic lustre. It is highly inflammable.

When potassium is placed in contact with sulphur in fusion, under the vapour of naphtha, they combine rapidly with the evolution of heat and light, and a grey substance, in appearance like artificial sulphuret of iron, is formed, a little sulphuretted hydrogen being evolved. The sulphuret of potassium is very inflammable; exposed to the atmosphere it absorbs oxygen and is converted into sulphate of potash; and when heated in the air, or when the union of the potassium and sulphur is effected in the atmosphere, inflammation takes place. Potassium inflames likewise when heated in sulphuretted hydrogen; hydrogen gas is disengaged, and sulphuret of potassium formed. Similar results are obtained from its action on phosphuretted hydrogen, but without inflammation: hydrogen is evolved, and phosphuret of potassium formed.

Gay-Lussac and Thenard suppose, that potassium combines with carbon; as when charcoal is dipt in dry potash in fusion, and exposed to heat, it acquires the property of inflaming on the contact of the air or of water.

With the metals potassium enters into combination. With mercury it produces some singular results. When One part of it is added to eight or ten parts of mercury in

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* Recherches Physico-Chimiques, tom. i, 176; ii, p. 235.

volume at 60° of Fahrenheit, they unite and form a substance like mercury in colour, but which has less coherence, for small portions of it appear as flattened spheres. When a globule is made to touch a globule of mercury about twice as large, they combine with considerable heat; the compound is fluid at the temperature of its formation ; but when cold it appears as a solid metal, similar in colour to silver. If the quantity of potassium is still further increased, so as to be about $\frac{1}{30}$ the weight of the mercury, the amalgam increases in hardness, and becomes brittle. The solid amalgam, in which the basis is in the smallest proportion, seems to consist of about one part in weight of base and 70 parts of mercury, and is very soft and malleable. When these compounds are exposed to air, they absorb oxygen ; potash is formed; and in a few minutes the mercury is found pure and unaltered. When a globule of the amalgam is thrown into water, it rapidly decomposes it with a hissing noise; potash is formed, hydrogen is disengaged, and the mercury remains free.

The fluid amalgam of mercury and potassium dissolves all the metals ; and in this state of union mercury acts on iron and platina, which in its pure state it does not do.

When potassium is heated with gold, or silver, or copper, it rapidly acts upon them; and when the compounds are thrown into water, the fluid is decomposed, potash formed, and the metals appear to be separated unaltered. An extensive series of experiments is given by Gay-Lussac and Thenard on the combination of potassium with the different metals *. In general they are decomposed slowly by the action of the air, oxygen being absorbed and potash formed, and they also suffer decomposition from the action of water.

It decomposes many of the metallic oxides with inflammation at the degree of heat at which it melts †, and if it

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* Recherches Physico-Chimiques, tom. i, p. 217.
† Nicholson's Journal, vol. xxiv, p. 92.

is in excess it combines with the reduced metal. By this kind of action it decomposes flint glass and green glass, reducing the metallic oxides they contain, and forming potash which dissolves the glass. At a red heat it acts even on the purest glass, attracting part of the oxygen of the alkali in the glass.

Potassium, by its attraction to oxygen, is a powerful agent in decomposing vegetable and animal substances, but can scarcely be applied to their analysis, from its causing new and complicated combinations of their elements.

POTASH.—Having stated the properties of the Base of Potash, the history of the alkali itself is to be delivered. The great source from which it is procured is the combustion of vegetable matter. In the mineral kingdom, it exists only as an ingredient of a few fossils, and in small quantity; and for the numerous purposes to which it is applied in the arts, it is always obtained by burning vegetables. The ashes are collected, and the saline matter is extracted from them by lixiviation with water; the solution is poured off from the undissolved matter, and is evaporated to a solid mass. This is the Pot-ashes of commerce; it is of a grey colour, and generally becomes humid from exposure to the air. When heated in a reverberatory furnace, the extractive matter it contains, and which appears to have been rendered soluble in water by the potash, is burnt out, and a portion of the water is dissipated. It then forms the Pearl-ash of commerce, which is of a white colour, frequently with a tinge of green or blue, arising, as Scheele shewed, from oxide of manganese, derived from the vegetable matter.

The product of saline matter is afforded in different quantities by different vegetables. In general, the harder woods afford more than the spongy, shrubs more than trees, and herbaceous plants the largest quantity. Even different parts of the same vegetable afford different proportions,

the branches affording more than the trunk, and the leaves more than the branches. It is also obtained in different states of purity with regard to the alkali. The general conclusions, from an extensive series of experiments on this subject, made by order of the French government, have been given by Pertuis, in a memoir, in which, as well as in one following it by Vauquelin, will be found much practical information * : 1st, Shrubs give three times, and herbaceous plants five times more ashes than large trees : 2d, The trunk of trees gives less ashes than the branches, and these less than the leaves : 3d, Plants in their state of maturity give more than they do either before or after that period : 4th, Plants burnt green give more than when they are weighed green but dried before they are burnt. Tables are given by Pertuis, of the products from a great variety of vegetables.

It is a question of some interest, whether the alkali pre-exists in the vegetable matter, or is formed during the combustion. It cannot be doubed but that part of it is derived from the former source, for plants contain salts having potash for their base, and these decomposed during the burning must furnish at least part of the saline matter obtained by the combustion. It is not, however, ascertained that the whole of what is obtained has had this origin. Nor do we know, whether the base of potash exists as an element of vegetable matter, and is oxidated so as to form the alkali during the combustion.

The pot-ash, or pearl-ash of commerce, is a very heterogeneous substance. The alkali is always combined with carbonic acid, and with this are present sulphate of potash, muriate of potash, siliceous earth, oxide of iron, and oxide of manganese. Different specimens differ in the quantities they contain of these ingredients. One pound

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* Annales de Chimie, tom. xix, p. 157, 194.

of the best pearl-ash was found by Kirwan to contain pot-
ash 3477 grains ; carbonic acid, 1290 ; water 414 ; sul-
phate of potash, 505 ; muriate of potash, 36 ; earth, 38 *.

To remove these impurities, the pearl ash is lixiviated
with a small portion of water, the alkali in combination
with carbonic acid is dissolved, while the others from their
more sparing solubility remain undissolved ; and by eva-
poration the former compound is obtained. Other pro-
cesses are also sometimes employed to obtain the alkali
more free from the admixture of foreign substances. The
one which is preferable is to expose the saline matter, na-
med White Tartar, to a red heat. It is a compound of
potash with a vegetable acid,—the Tartaric acid. This
acid is decomposed by the high temperature, and a quan-
tity of carbonic acid is formed from its decomposition,
with which the potash remains combined. This is freed
from any insoluble matter by lixiviation with water, the
ley is evaporated in a clean iron bason, and a white granu-
lar powder is obtained, formerly known by the name of
Salt of Tartar. A similar product is obtained from the
deflagration of nitre with charcoal, or by exposing to a red
heat a mixture of equal quantities of nitre and white tar-
tar. All these, though purer than the pot-ash or pearl ash
of commerce, are still contaminated with some foreign
substances, especially with some earths and a little sul-
phate of potash.

Different methods are followed to abstract the carbonic
acid, and obtain the alkali pure. The following is the
one generally employed, and which is still a preliminary
one to others, requisite to obtain it in a state of perfect
purity. To the purified pearl-ash of commerce, or to any
of the analogous substances obtained by the processes just
described, twice the weight of quicklime in powder is add-

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* Transactions of the Irish Academy, 1789, p. 10.

ed ; on this is poured as much water as is requisite to
slake the lime ; an additional portion of water is then add-
ed, so as to give the materials a thin consistence, and the
mixture without being exposed to heat, is allowed to stand
for some hours, agitating it occasionally. The whole is
poured into a glass funnel, the tube of which is obstruct-
ed with a piece of linen ; the fluid part soon begins to fil-
trate through the mass, colourless and transparent ; fresh
portions of water are poured on the matter in the funnel,
and this is continued until 8 or 10 times the weight of
the potash originally employed have passed through the
filtre.

In this process the lime attracts the carbonic acid from
the potash ; and the alkali is dissolved by the water. It
is not, however, perfectly pure. There are no adequate
means employed to separate the sulphate and muriate of
potash ; even a portion of the siliceous earth is held in
combination by the alkali ; and the whole of the carbonic
acid is not abstracted, for when the greater portion has
been removed by the affinity exerted towards it by the
lime, the quantity of the potash adds so much to the force
of its affinity, that a proportion of the acid is still retained
in combination with it. The greater part of this carbonic
acid, as well as any sulphuric acid, may be abstracted by
a solution of the earth named barytes, and this affords an
easy mode of obtaining potash, so far pure.

The process generally followed, however, is one disco-
vered by Berthollet, founded on the solubility of pure pot-
ash in alkohol, while the other substances are insoluble.
The first stage of the process is that which has just been
described. The liquor obtained by the filtration is eva-
porated until it become of a thickish consistence, and there
is added to it about an equal weight of alkohol, allowing
it to stand for some time in a close vessel. A quantity of
solid matter, in part crystallized, is collected at the bot-

tom; this is carbonate of potash, with other saline substances, and a little silica, lime, and oxide of iron. Above this is a small quantity of a very dark-coloured fluid; this is the water of the alkohol with part of the alkali combined with carbonic acid. Floating above this, is another fluid of a lighter colour, which is a solution of potash nearly pure in alkohol; it is to be evaporated quickly in a silver bason placed in sand; a vessel of glass, or of almost any metal but silver, being acted on by the alkaline solution. The liquor, after a moderate evaporation, on being allowed to remain at rest, separates into two fluids: the heavier one, which is in small quantity, is a solution of the alkali still combined with carbonic acid: the lighter one above it is the solution of the pure alkali in alkohol; it is to be poured off, and again evaporated with a quick heat. On allowing it to remain for a day or two in a close vessel, it deposites transparent crystals of potash, or, if evaporated until a pellicle appear on its surface, on cooling, the potash passes into a concrete state without a regular crystallization; in either case, a quantity of deep-coloured liquor separates, which is to be poured off; and the alkali preserved carefully secluded from the air *.

Another process more economical has been pointed out by Lowitz, which may be employed where it is not requisite to have the alkali in a state of complete purity. The solution prepared as before from the mixture of the potash of commerce with lime is evaporated until a thick pellicle appear on its surface: It is allowed to cool, and a quantity of matter, which is deposited, consisting of the foreign salts mixed with the potash, is to be removed. The liquor is again to be evaporated, and the pellicle which forms on its surface is to be skimmed off as it accumulates. When this ceases to be produced, and the matter does not boil up, it is to be removed from the fire and allowed to

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* Mémoires de l'Acad. des Sciences, 1783, p. 408.

cool with constant agitation. It is then to be dissolved in twice its weight of cold water, and the solution is evaporated, until it begin to deposite crystals. If it should consolidate without crystallizing, a small quantity of water is to be added, and the mass heated again to render it fluid. By successive crystallizations, the liquor is left of a brown colour, which is owing to carbonaceous matter suspended in it; and when this has been deposited by rest, the clear liquor may be evaporated and crystallized as long as the crystals are obtained colourless *. By this process, the different salts are nearly separated from the potash; but part of the earthy matter probably remains. Dr Kennedy, however, who gave a process for the preparation of pure potash nearly the same with that of Lowitz, observed, that in saturating the potash thus procured with an acid, there appeared no trace of any earth, and that by the most delicate tests of sulphuric and muriatic acids, no portions of these acids are discoverable in it †. Mr Chenevix, on the other hand, affirms, that minute portions of silica, alumina, iron and carbonic acid, may always be detected in the potash prepared by this method, while there are no traces of them in that prepared by Berthollet's process. The one process might be employed with advantage, as preliminary to the other.

Potash is a solid substance of a white colour, crystallizable from its saturated solution either in water or alkohol. The figures of the crystals are, according to the extent of evaporation, in thin plates, or in slender needles, and when more slowly formed, in tetraedral pyramids, or in octaedrons. They contain various proportions of water of crystallization; those which are slowly formed, and of a regular figure, contain about 0.43. They produce cold in dissolving in water, while the solution of dry un-

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* Nicholson's Journal, 4to, vol. i, p. 164.
† Edinburgh Philosophical Transactions, 1799.

crystallized potash is attended with an elevation of temperature.

When potash is exposed to heat, it fuses, and a portion of watery vapour is disengaged from it; this ceases, and when the temperature is reduced, the potash forms a solid mass. The melting point of this is about 360, and by any farther increase of heat, no more water can be expelled from it; it flows smoothly, and if the heat be raised, the potash rises in white vapours without any separation of water. It was then supposed to be the alkali free from water; but from farther investigations, it appeared that it retains a large portion in combination with it.

D'Arcet discovered this combination of water with the fixed alkalis, first with regard to soda, by observing, that in combining an acid with subcarbonate of soda, the quantity of the acid neutralized considerably exceeded that neutralized by a quantity of fused soda, equivalent to that existing in the subcarbonate, considering the fused soda as real soda. The deficiency therefore could be ascribed only to the presence of water in the fused soda: the quantity he estimated at 28 or 29 in 100. From experiments of the same kind, he inferred, that fused potash contains 27 or 28 of water in 100 [*]. About the same time, Berthollet had observed a considerable difference in different specimens of the alkaline earth named Barytes, in neutralizing an acid, and this he found to be owing to water being combined with it in some modes of preparing it, and not in others. From this he suspected the presence of water in potash. By combining potash with muriatic acid, finding the weight of the ignited salt, and ascertaining the quantity of muriatic acid it contained, he found, that 100 parts of potash, which have been kept in fusion, retain 13.64 of water; and from a subsequent experiment, he fixed the proportion at 13.89. He farther established the existence of combined water in fused pot-

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[*] Nicholson's Journal, vol. xxvii, p. 31.

ash, by exposing it to heat with iron-filings; a large
quantity of hydrogen gas was disengaged *.   Berard, in
some observations on D'Arcet's experiment, pointed out
the influence of some circumstances, particularly in his
mode of estimating the quantity of carbonic acid in the
subcarbonate, which would lead to the proportion of wa-
ter being estimated rather too high; and by obviating
these, he fixed the proportion at 0.20, and from a differ-
ent mode, similar to that of Berthollet's, at 18.86 †.   Cur-
audau, from the loss of weight sustained in exposing to
heat potash, with siliceous earth which had been previous-
ly heated for two hours in a forge fire, assigned the quan-
tity of water at 27.5 *per cent* ‡.   Sir H. Davy, from the
same experiment, inferred it to be about 16 or 17 *per
cent.*; and from the loss of weight in heating fused potash
with boracic acid that had been ignited, the proportion
appeared to be from 19 to 20 *per cent* §.   Berzelius fixed
the proportion at 16.1 *per cent.*, and this accords with the
law, that the proportion of combined water in hydrates
has a relation to the oxygen in the oxide which is the base
of the hydrate, the oxygen in this quantity of water being
the same as the oxygen in the real potash.

Potash then, in its insulated state, is a Hydrate; that is,
according to the common doctrine, a definite compound of
a base, called the real alkali, with water. According to the
doctrine I have illustrated, the elements of water exist in
its composition; or it is a ternary compound of potassium,
oxygen, and hydrogen; and its high degree of alkaline
energy may, in conformity to the same doctrine, be ascri-
bed to the influence of the two latter elements.   Admit-

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* Mémoires d'Arcueil, t. ii, p. 50.
† Nicholson's Journal, vol. xxvii, p. 351.
‡ Journal de Physique, tom. lx, or Retrospect of Disco-
veries, vol. vi, p. 246.
§ Philosophical Transactions 1811.

ting the above proportion of combined water, its composition will be 70 of potassium, 28.1 of oxygen, and 1.9 of hydrogen.

The real alkali is supposed to be obtained by burning potassium in oxygen gas, and heating the product to redness, so as to expel the excess of oxygen. It is of a greyish-green colour, if the combustion has been on platina; if on glass, the colour approaches to white: it is harder than common potash, and appears to be of a greater specific gravity: its fracture is vitreous. It requires a strong red heat for its perfect fusion, and evaporates slowly by a farther rise of temperature. When a little water is added to it, it heats violently, becomes white, and is converted into the hydrate, which is more fusible and volatile *. It is uncertain what are the powers of the compound in the former state, whether it has any alkaline quality or not; for it cannot be submitted to examination without the admission of water, which immediately changes its composition.

Potash, it has been stated, combines with an additional proportion of water, when it exists in the crystallized state. This probably constitutes the proper hydrate. It has farther so strong an attraction to water, that it absorbs it with avidity, until it pass into a state of solution. It acts rapidly on ice, and liquefies it with the production of intense cold. It also imbibes water rapidly from the atmosphere, and is a powerful agent in abstracting it from gases. It requires less than its own weight of water for solution; one part at 60° dissolves two parts, the liquid being dense and of an oily consistence.

Potash is capable of uniting with oxygen. Gay-Lussac and Thenard state, that when it is exposed in a crucible of silver to a red heat, in contact with the air, it acquires in a few minutes a deeper colour, and passes to the

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* Davy, Philosophical Transactions, 1811.

state of the oxide at the maximum, so that when water is
added it gives out oxygen and returns to the state of pot-
ash *. The result therefore is the decomposition of the pot-
ash, and the combination of the potassium with an addition-
al proportion of oxygen. If the observation be correct, the
inferior neutralizing power of ignited potash to that of the
real alkali, indicated by the experiments stated above, can-
not be ascribed entirely to the presence of water, but must
be owing in part to the excess of oxygen combined with it.

Potash is extremely caustic : it quickly erodes the skin,
and mixed with animal matter, it completely dissolves it,
occasioning, at the same time, its decomposition. From
its action on the skin it has a soapy feel. It combines with
oils and fats, forming saponaceous compounds of a soft
consistence.

A very minute quantity of it changes the vegetable co-
lours to a green.

Potash acts with considerable energy on the simple in-
flammables, at least on phosphorus and sulphur. Char-
coal it seems merely to dissolve in small quantity, with-
out any marked change of properties.

The combination with phosphorus is effected by expo-
sing them to heat in a close tube; but as the influence of
water can scarcely be entirely excluded, it influences the
results ; it suffers decomposition, its oxygen combines
with one portion of phosphorus, forming phosphoric acid,
which unites with the alkali, and its hydrogen with ano-
ther portion of phosphorus forms phosphuretted hydro-
gen. These actions are exerted even when a solution of
potash, not very highly concentrated, is boiled on phos-
phorus.

With sulphur potash combines with facility. When
equal weights of them are exposed to heat in a crucible,

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* Recherches Physico-Chimiques, tom. i, p. 167.

they enter into fusion, and at the same time into chemical union. When cold a substance is obtained, hard and brittle, of a dark reddish-brown colour, which from its resemblance to the liver of an animal gave origin to the name of Hepar Sulphuris, applied by the older chemists to these compounds. A similar combination is obtained, by exposing to heat one part of sulphur with two parts of subcarbonate of potash, the sulphur and the alkali uniting, and the carbonic acid being expelled; but the combination is less intimate, probably from part of the carbonic acid being retained; the colour is only grey or green. From some late experiments by Vauquelin and Gay-Lussac, it appears, that when the sulphur and potash are exposed to a red heat, part of the oxygen of the alkali is transferred to the sulphur, so as to form sulphuric acid, and of course a portion of sulphuret of potassium is formed. When they are submitted to a lower heat, they merely combine together [*].

Sulphuret of Potash is inodorous while it remains dry; it is only when moistened or dissolved that it acquires a fetid smell, from the production of sulphuretted hydrogen. It is fusible; and when exposed to a strong heat in close vessels, a portion of sulphur is sublimed from it, without any sulphuretted hydrogen, while a portion of this gas is obtained, if the sulphuret has been previously moistened [†]. Exposed to the air, it attracts humidity, especially that which has been prepared with pure potash, probably from an excess of alkali. When dissolved in water it suffers decomposition, a portion of the sulphur attracting oxygen so as to form sulphuric acid, which is saturated by part of the alkali, and the hydrogen of the decomposed water combining with the rest of the sulphur so as to form super-sulphuretted hydrogen, and establish a sulphuretted hydro-sulphuret, as has been already stated. From the sul-

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[*] Annales de Chimie et Physique, tom. vi, p. 321.
[†] Mémoires de l'Acad. des Sciences, 1786, p. 58.

phuret always suffering change when in a state of solution, it is scarcely possible to discover its peculiar agencies. One singular property belonging to it is, that when fused with some of the metals, with gold for example, a combination is formed, which is soluble in water.

When sulphuretted hydrogen gas is transmitted through a solution of potash they combine together, and a compound is formed, HYDRO-SULPHURET OF POTASH, which has unequivocal saline properties : the alkali being neutralized by the acidity of the hydro-sulphuretted acid. This salt was more particularly examined by Vauquelin [*]. It is white and transparent, resembling by its transparency, and the size of its crystals, sulphate of soda. Their form is a tetraedral prism acuminated with four planes, and an hexaedral prism acuminated with six planes. Its taste is at first alkaline, and afterwards bitter ; when dry, it is inodorous ; but when liquid, it exhales a fetid odour. It attracts humidity from the atmosphere ; when fluid, it gives a green colour to bodies in contact with it. It is soluble both in water and in alcohol, producing cold in its solution : with acids, it gives rise to a brisk effervescence, without depositing sulphur.

SULPHURETTED HYDRO-SULPHURET OF POTASH, it has been stated, (p. 284.) is formed either when sulphur is boiled with hydro-sulphuret of potash, or with a solution of potash. It is usually obtained in the latter mode ; it is of a yellow colour, of various shades, from its state of concentration, and from variations in the proportions of sulphur. Its taste is nauseous and acrid, it has a soapy feel, and stains the cuticle black. It is decomposed by the acids, which precipitate the sulphur white or of a pale yellow, and disengage a portion of sulphuretted hydrogen gas. By long exposure to the air, the sulphur, absorbing oxygen, passes to the state of sulphuric acid.

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[*] Annales de Chimie, tom. xlii, p. 40.

Potash does not in general act with much energy on the metals. There are some of them the oxidation of which it promotes when heated with them in contact with the air. Thus, it cannot be heated to redness in a platina crucible without acting on the metal by this effect; and it is equally powerful in promoting the oxidation of iridium and osmium. It combines also by fusion with a number of the metallic oxides, and with some of them unites even in the humid way.

It acts with considerable energy on the greater number of the earths by fusion; with siliceous earth it forms a perfect glass, and when in larger proportion a compound which is soluble in water. With the others, it forms frits or enamels. Even in solution in water, it dissolves alumina and glucine.

Its most distinctive property, in common with the other alkalis, is its power of combining with and neutralizing the acids. It is inferior in this power to ammonia and soda, a larger quantity of it being requisite to saturate a given quantity of acid: this, according to Berthollet's views, indicates a less energetic action; yet it decomposes the ammoniacal salts, which he ascribes to its greater fixity: It also decomposes several salts of soda, which is ascribed to the greater tendency of cohesion of the salts of potash.

The salts of potash have scarcely any striking generic characters; they are all soluble in water, and are in general crystallizable. Added to a strong solution of sulphate of alumina, they cause a formation of alum in crystals; from the addition of tartaric acid, they afford a granular precipitate of super-tartrate of potash; and they throw down a reddish yellow precipitate from a solution of muriate of platina. Their acid cannot be expelled by heat, unless it suffer at the same time decomposition from the high temperature.

CARBONATE OF POTASH.—Potash combines with carbonic acid with great facility. The combination, it appears, can

be established like that of the other alkaline carbonates in
two definite proportions, in the one of which the quantity
of carbonic acid combined with a given weight of base is
twice that combined in the other.   The compound with
the smaller proportion of carbonic acid retains the dis-
tinctive alkaline properties ; it is therefore a Subcarbonate ;
in the other, which for distinction has been named, from
the double proportion of acid which it contains, the Bi-
carbonate, they also remain to a certain extent. It is doubt-
ful, therefore, if there exist any definite compound, in which
carbonic acid produces perfect neutralization of the alka-
line properties.

The first of these compounds, SUBCARBONATE OF PO-
TASH, is the basis of the potash and pearl-ash of commerce,
being formed in the incineration of wood ; it is obtained
from the residual ashes by lixiviation of water, and eva-
poration : and hence has an intermixture of the other sa-
line substances formed or evolved in the same process.   It
accordingly always contains portions of sulphate and mu-
riate of potash, silica and alumina, and generally of oxides
of manganese and iron.

To remove these, as to obtain the purer subcarbonate,
the common pearl-ash, after being calcined at a low red
heat, is dissolved in an equal weight of warm water, the
clear solution is poured off from the undissolved matter,
and is evaporated in a clean iron or silver bason until a pel-
licle appear on its surface ; it is removed and allowed to
stand for some hours, when a little of the foreign salts is
deposited ; the clear liquor is poured off, and is evaporat-
ed to a dry mass.   Another process for preparing it, for-
merly much employed, is that of burning the salt, known
by the name of Tartar, which is deposited from wines in
the cask, and which consists of potash united with a vege-
table acid, the Tartaric.   This acid having carbon and hy-
drogen for its base, a portion of carbonic acid is formed in
the decomposition it suffers at a high temperature, which
remains combined with the alkali, forming a subcarbonate.

This is separated from the carbonaceous matter by solution in water, and by evaporation is obtained in a concrete state. From being prepared in this way, it was formerly named Salt of Tartar. It was also obtained sometimes by deflagrating the tartar with nitrate of potash ; or by deflagrating nitre with charcoal, the nitric acid being decomposed in the deflagration, and carbonic acid formed which is attracted by the potash. As obtained by these processes, the subcarbonate is purer than as obtained from the pearl-ash of commerce, the latter always containing sulphate of potash and siliceous earth : and according to Dr Black, it contains a larger quantity of carbonic acid [*].

The subcarbonate of potash purified by solution in wa-

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[*] It is an object of some importance in practical chemistry to determine by an easy mode the quantity of alkali in an active state, in the potashes of commerce, and also in some cases, such as for the manufacture of alum, the quantity of it combined with sulphuric and muriatic acids. Kirwan gave a method founded on the precipitation of alumina from alum by the alkaline carbonate, but it is very defective. Vauquelin proposed a formula founded on the neutralization of the alkali by nitric acid, (Annales de Chimie, t. xl, p. 234.), and the precipitation of the sulphuric acid by nitrate of barytes, and of muriatic acid by nitrate of silver ; but it is rather complicated. The easiest mode is to ascertain the quantity of sulphuric acid of the usual specific gravity, which a given weight of the potash neutralizes. If the object be to ascertain the quantity of alkali combined both with sulphuric and carbonic acids, the portion in the latter state may be neutralized by sulphuric acid, and the whole of this acid which is present may be precipitated by nitrate of barytes ; the quantity of sulphate of barytes will give the quantity of sulphuric acid, and this again will give the quantity of potash, according to the known composition of these compounds; and after this the quantity of muriate of potash may be ascertained by precipitation by nitrate of silver. Another method more minute has been given by Descroizilles, (Annales de Chimie, t. lx.).

ter, and obtained in a concrete state by evaporation, is in
the form of coarse grains, of a white colour. It is not
susceptible of regular crystallization. From the excess of
alkali it contains, it is deliquescent ; if exposed to the air,
it becomes humid, and soon attracts as much water as dis-
solves it. It dissolves in rather less than its own weight of
water at 60°. Its taste is acrid ; it changes the vegetable
colours to a green, and combines with oils, forming a sa-
ponaceous compound. It is decomposed by the acids ; its
carbonic acid being disengaged with effervescence. A con-
siderable portion, but not the whole of its acid is expelled
by a strong red heat.

According to Kirwan, common subcarbonate of potash
contains about 60 of alkali, 28 or 30 of carbonic acid, and
6 of water, with a few grains of siliceous earth, sulphate of
potash, and argil. The pure subcarbonate consists, accord-
ing to the estimate by Berard and by Dulong, of 70 of
alkali, and 30 of carbonic acid. Dr Wollaston gives the
proportions of 68.3 with 31.7, or 100 with 46.5.

BI-CARBONATE OF POTASH.—This was obtained by the
older chemists by exposing subcarbonate of potash to the
air until it passed into solution, and leaving the solution
exposed for a number of months ; carbonic acid was slow-
ly attracted from the atmosphere, and crystals were depo-
sited. It can be obtained more speedily by exposing a so-
lution of the subcarbonate to an atmosphere of carbonic
acid, such as that collected over the surface of ferment-
ing liquors, or by passing through it a current of this
gas, disengaged from marble, and diluted sulphuric acid,
interposing a bottle with water, to detain any minute
quantity of sulphuric acid that might be elevated by the
violence of the effervescence. In either case the solution
ought to be of such a strength (one part of subcarbonate
to three of water) that when saturated it crystallizes spon-
taneously, as the crystallization cannot be promoted by e-
vaporation, a heat not greater than that of boiling water

partially decomposing the salt, and disengaging a little carbonic acid. As the saturation proceeds, a light earthy precipitate is formed, consisting, as Pelletier has shewn, of silica that had been combined with the alkali. Another process was given by Bergman ;—mixing a solution of subcarbonate of potash with a solution of carbonate of ammonia in a retort, and applying heat; the ammonia is expelled, and the potash saturated with carbonic acid crystallizes as the liquor cools. I have already remarked, that though this salt is usually considered as the neutral carbonate, it retains very obvious alkaline properties.

Its crystals are bevelled quadrangular prisms ; they do not, like the subcarbonate, deliquesce. They require, at a mean temperature, four parts of water for their solution, and produce, while dissolving, a degree of cold. They are much more soluble in hot water, the water taking up even $\frac{5}{6}$ of its weight ; but if the temperature be that of boiling water, part of the carbonic acid assumes the elastic state, and rises through the liquor. Exposed to a moderate heat in a dry state, the crystals split, then fuse, part with their water of crystallization, and yield part of the carbonic acid. The taste of this salt is much more mild than that of the sub-carbonate ; it has no causticity ; but it unites with oils, and changes the vegetable colours to a green. Pelletier gave, as the proportions of its elements, 40 of potash, 43 of carbonic acid, and 17 of water, and the proportions by Kirwan are almost precisely the same. According to Berard it is composed of 48.9 of potash, 42.1 of acid, and 9 of water. According to Dr Wollaston, of 47.1 of potash, 43.9 of acid, and 9 of water : abstracting the water in the latter, the proportion is 51.8 with 48.2, or 100 with 93, twice the quantity existing in the subcarbonate.

It is decomposed in the humid way by lime, barytes and strontites, which attract the carbonic acid, forming insoluble precipitates. In the dry way, and with the assistance of heat, silica decomposes it, combining with the alkali, and forming a glass, the carbonic acid being expelled. It is

also immediately decomposed by the acids, which disengage the carbonic acid gas with a rapid effervescence.

Potash appears capable of combining with a portion of carbonic acid, inferior to that in the preceding compound, so as to form a crystallizable salt. It is remarked by Steinacher, that if the saturating of the solution of the sub-carbonate with carbonic acid be stopt, when the siliceous earth appears to be deposited, the liquor evaporated by a gentle heat affords crystals in plates, which so far differ from the other crystallized salt as to deliquesce.

The alkali can be super-saturated with carbonic acid, by impregnating the solution more strongly by the assistance of cold and pressure. The taste of this solution is plea-santly acidulous, with some pungency, and the alkali thus supersaturated proving less irritating to the stomach : it has been employed in medicine. Different kinds of apparatus have been employed to prepare it, particularly that invented by Dr Nooth, described in the 65th volume of the Philosophical Transactions. It may also be prepared in a range of Woulfe's bottles, in which, by a sufficient immersion of the tubes in the liquid, the necessary pressure is obtained : and other kinds of apparatus, in which still greater pressure can be applied, so as to bring a larger quantity of carbonic acid into combination, are employed by some chemical artists.

NITRATE OF POTASH. This is the well-known salt Nitre or Saltpetre, so extensively used. It occurs as a natural or spontaneous production in certain situations, in warm and dry climates. In India it is mixed with the soil, and is extracted by washing the earthy matter with water, and evaporating the solution ; it is obtained in irregular crys-tals, and in an impure state. The nitre used in this coun-try is derived from this source. There are many other natural situations in which nitre is spontaneously formed.

It is also procured by an artificial process, which is ex-tensively conducted in France and Germany. The refuse

of vegetables, together with various animal matters, such as blood, and other excrementitious substances, are mixed with carbonate of lime, old plaster, or other materials containing calcareous earth. The mixture is laid in heaps in ditches protected from the rain by sheds, but open at the sides. In these nitre beds, as they are named, the materials are allowed to remain for some months, being turned up occasionally to present a new surface to the atmosphere. They are then washed, and a considerable quantity of the salts formed by the union of nitric acid with lime and potash are extracted.

The theory of this process, in which nitric acid is formed, was not understood until elucidated by the discoveries of modern chemistry. The experiments of Messrs Thouvenel first threw light on the process, by establishing the principal facts connected with it; and the discovery by Cavendish of the composition of nitric acid completed the theory. The following is an outline of the general facts, from Thouvenel's memoir.

They imitated the common process, and examined the influence of different circumstances on the formation of the nitre. When animal and vegetable matters were mixed with calcareous earth, and exposed to the air in large earthen or glass vessels, nitre was formed. If the calcareous earth was kept out, there was no formation of nitre, not even when either of the fixed alkalis was substituted for it. When magnesia or argillaceous earth was used, the quantity was very inconsiderable; even quicklime did not answer the purpose, but in order to obtain the proper effect, it was necessary that it should be in its mild state, or combined with carbonic acid. It was likewise found, that if the putrefying matter was in a separate vessel, and the air arising from it were washed in lime water, or in a solution of caustic kali, before being brought into contact with the carbonate of lime, the formation of nitre ceased. Different animal substances produced different quantities

of nitre; blood gave most; and the production of it was also different at different periods of putrefaction. The presence of atmospheric air is indispensable to the process, or nearly so, since, when it was excluded, and the vessels contained only the putrid effluvia, no nitre was formed; at the same time, if the air was agitated, or frequently renewed, the production was rather lessened. The presence of moisture is likewise favourable to its production, as it is more abundantly formed in damp places than where the air is dry. Too much humidity, however, is hurtful. Lastly, the presence of a quantity of nitre, or of nitrate of lime, already formed, appears to render the farther formation more rapid. This, however, is only to a certain extent; for after a certain quantity of nitrous salts is formed, the process stops, but if they are extracted by washing, it again commences on exposing the materials to the air *.

It may be difficult to explain precisely the operation of all these circumstances In general, it may be observed, that during the putrefaction of the animal matter, nitrogen gas is disengaged, which being presented to the oxygen of the atmospheric air in a nascent state, combines with it, and forms the nitric acid. The vegetable matter moderates the putrefaction of the animal matter, prevents the formation of ammonia, and perhaps furnishes a quantity of oxygen, with which the nitrogen combines. The utility of the lime is best explained on the principle of its disposing affinity to oxygen and nitrogen, in consequence of which it brings them into combination, and attracts the nitric acid that is formed. The superiority of the carbonate of lime over pure lime seems to arise from the circumstance, that the pure lime acts too strongly on the animal matter, combines with part of it, and resolves the rest into ammonia, while the action of the carbonate is less

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* Journal de Physique, tom. xxix, p. 264.

energetic and more slow. Potash and soda act in the same manner as lime, and are therefore equally unfit for the process. The utility of moisture seems owing to its absorbing and detaining in some measure the disengaged gases, and diffusing through the materials the nitrous salt when it is formed. Some have imagined that water is decomposed, and furnishes oxygen to the nitrogen of the animal matter; but, if this were the case, the presence of atmospheric air would not be necessary, and during animal putrefaction, nitric acid would always be formed.

It appears, then, that the circumstances more directly concerned in the process, are the presence of animal matter, and the action of atmospheric air and of carbonate of lime. Nitrogen gas is discharged from the former, and the lime by a disposing affinity effects its combination with the oxygen of the atmospheric air. There is some reason to believe, that under certain circumstances carbonate of lime alone is able, by its action on the nitrogen and oxygen of the atmosphere, to cause them to combine and form nitric acid; since it has been found that calcareous rocks, at a great height, and at a distance from animal effluvia, have been encrusted with nitrate of lime. An interesting account of the Nitre caves of Kentucky, in which there is this natural formation of nitre to a great extent on the surface of limestone, without any apparent source of animal effluvia, is given in the sixth volume of the American Philosophical Transactions. The formation of nitre, however, is always more abundant where animal effluvia are present, and takes place even where the other arrangements of nitre beds are not present. Thus it often appears as an efflorescence on the walls of stables, and of old buildings which are protected from too much humidity.

Experiments appear to render it probable, that a quantity of potash is formed in this process which combines with the nitric acid; and the vegetable matter has been supposed to contribute to its formation, or rather may

yield it ready formed. The alkali appears even to be ele-
vated in the vapour of the putrefying matter ; as well-
washed chalk, it was ascertained both by Chaptal and
Thouvenel, yielded nitre after having been exposed to the
effluvia of putrefying substances for some months.

The nitrate of lime, and the nitrate of potash, which are
formed by the process now described, are extracted by
washing the materials with water. A quantity of wood
ashes is added to the liquor, the potash of which decom-
poses the nitrate of lime, by attracting the nitric acid ; and
the nitrate of potash thus formed, together with the quan-
tity of it originally contained in the solution, are obtain-
ed by evaporation and crystallization. The salt is at first
impure, having an intermixture particularly of sea salt or
muriate of soda, which appears to be formed along with
the nitre and always to accompany it. From this it is pu-
rified by a second or a third solution in boiling water, and
subsequent crystallization.

A full view of the process, particularly in what relates
to the practice, was drawn up by Chaptal at a period when
the production of nitre was of much importance to France,
and published, as well as a new process which was carried
into practice, of refining the nitre [*].

Nitrate of potash affords a good example of the difficul-
ty of determining with accuracy the proportions of the con-
stituent parts of salts. It consists, according to Kirwan,
of nitric acid 44, potash 51.8, and water of composition
4.2 ; according to Berthollet, abstracting the water of cry-
stallization, of 41.3 of acid, and 58.7 of potash; to The-
nard, of 40.5 of acid, and 59.5 of potash ; according to
Richter 46.7 of acid, and 53.3 of potash ; and according
to Langier of 38 and 62. Much of this diversity, how-
ever, arose from the fact of the presence of water in fused

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[*] Annales de Chimie, tom. xx, p. 308.   Nicholson's Jour-
nal , 4to, vol. ii, p 23.

potash not being known ; and the uncertainty, too, whether nitre retains in its crystals any water of crystallization. It now appears that nitre contains no water. The proportions given by Berard are 51.36 of acid, and 48.64 of potash : those by Dr Wollaston from a synthetic experiment are 53.3 of acid, and 46.7 of base.

Nitre crystallizes in six-sided prisms acuminated by six planes, often perforated, and of considerable size, sometimes also in a dodecahedron formed of two six-sided pyramids, joined by their bases ; its taste is cool and penetrating ; it is soluble in seven parts of water at the temperature of 60, and in an equal weight of boiling water ; the latter solution crystallizing upon cooling. In evaporating its solution, it has been said that part of the salt is carried off, from its affinity to the water ; and Lavoisier stated the proportion as even considerable, but the fact has been denied by Riffault. It melts by a moderate heat into a transparent fluid, which when cold forms a white semitransparent mass. If the heat be continued, a partial decomposition of the acid takes place, and the salt is converted into nitrite of potash. The oxygen expelled in this stage is nearly pure. By a farther application and increase of the heat, the nitrite is also decomposed by the decomposition of the acid, the oxygen and nitrogen of which are separated from their chemical combination, and pass off in the gaseous form ; the oxygen therefore last disengaged is less pure than that towards the middle of the process. The decomposition appears to be aided when it is performed in an earthen retort, by the affinity of the alkaline base of the nitre to the earthy matter ; and accordingly, the potash is found in combination with silica, forming a gelatinous solution when water is added to it. It likewise takes place in a glass retort, but less air is obtained [*] ; in an iron retort the air obtained is less pure. These facts, with

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[*] Ehrman, Essai d'un Art de Fusion, p. 23.

regard to the decomposition of nitre by heat, were prin-
cipally ascertained by Berthollet *. He states the quanti-
ty of air obtained at from 550 to 580 cubic inches from
one ounce of nitre; Cavallo obtained 750 cubic inches;
and Ehrman from 7 to 800. From 100 grains of nitre
heated in an iron tube Dalton obtained about 30 grains
of air, which being received in successive portions, the
first contained 70 *per cent.* of oxygen, the last only 50. As
potassium can combine with a larger proportion of oxy-
gen than what exists in potash, it may be expected, that
in this process of the decomposition of nitre by heat, in
which oxygen is presented to it under favourable circum-
stances, this higher degree of oxidation will be establish-
ed. Gay-Lussac and Thenard have accordingly found
that this is the result, especially when the nitrate quite dry
is exposed to a strong heat †.

The action of nitre on inflammable substances has al-
ready been considered when treating of deflagration; as
its acid is so easily decomposed, and as it contains so large
a quantity of oxygen, it excites a rapid combustion. Ac-
cordingly sulphur or charcoal mixed with an equal weight
of nitre, and thrown into an ignited crucible, is rapidly
oxygenated, and much heat and light extricated; the re-
siduum is the compound of the oxidated product with the
potash. When it is deflagrated with charcoal, a pure sub-
carbonate of potash is obtained, and this process has been
often followed by the chemists, to prepare that salt. When
exposed to heat with three parts of the salt named tartar,
which consists of potash and a particular vegetable acid,
the tartaric, both acids are decomposed, and the residuum
is carbonate of potash mixed with a quantity of charcoal
derived from the tartaric acid. This, as being employed
to promote the fusion of earthy and metallic substances,

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* Mémoires de l'Acad. des Sciences, 1781, p. 3.
† Recherches Physico-Chimiques, tom. i, p. 168.

has been named Black Flux. The White Flux, which is merely a subcarbonate of potash, is formed by treating in the same way equal parts of nitre and tartar.

On this property of nitrate of potash is established the composition of Gunpowder, which owes to this salt its detonating quality. It consists of about 75 parts by weight of nitre, 15 or 16 of charcoal, and 9 or 10 of sulphur. The nitre is employed in its purest state, and is previously fused to expel any water of crystallization: the charcoal is prepared from wood decomposed in iron retorts. The materials are separately ground to a fine powder, and are then mixed together; the mixture is ground under two stones placed vertically, and made to move on a flat stone; a small quantity of water being added to prevent the powder from flying off in dust, and to lessen the risk of explosion. It is brought at the end of the trituration to a stiff consistence; this, after being dried a little, is broken down and pressed through a sieve, by which it is granulated, and by causing these grains to rub against each other, in barrels kept revolving, they are rounded and glazed, and are at length dried *.

The general theory of the action of gunpowder is obvious. The particle of it on which the spark struck by the flint from the steel falls, is immediately heated to the temperature of ignition, or near it; the nitre is decomposed, and its oxygen combines with the sulphur and charcoal, which are likewise heated. This combination extricates as much heat as is sufficient to inflame successively, though rapidly, the remaining mass. The cause of the great expansive force of the gunpowder, when inflamed in a confined space, is the sudden production of nitrogen, sulphurous acid, and carbonic acid gases, their elasticity being augmented by the large quantity of caloric which is

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* A full account of the process, as carried on in England, is given by Mr Coleman, Philosophical Magazine, vol. ix.

extricated. The influence of the high temperature from
the deflagration in augmenting the elasticity, is very well
shown in an experiment by Rumford, in which gunpowder
was fired under the pressure of a great weight. When, by
sufficient pressure, the elastic fluid was confined, after ha-
ving been generated, for a few minutes or even a few se-
conds, the expansive force it exerted was far from being
considerable.

From this explanation of its mode of operation, it is ob-
vious, that next to the proper proportion of the ingredi-
ents, its power will depend on their proper mixture. The
more finely the nitre is divided, and intimately mixed with
the sulphur and charcoal, the combustion will be more in-
stantaneous, the production of the gases from a certain
quantity of it will be greater in a given time, and the ex-
pansive force will be augmented. Hence the damage
which gunpowder receives from moisture, as the nitre be-
ing soluble in water, is separated more or less from the
other ingredients. It is from this cause, too, that the gra-
nulation of the powder, though it renders it more conve-
nient for use, weakens its power. Even in the best state
of preparation, it appears from Rumford's experiments,
that much of the gunpowder fired in a confined space is
thrown out without being sufficiently kindled. The prin-
cipal use of the sulphur in gunpowder seems to be, to ren-
der it more easily inflamed, as it combines with oxygen at
a lower temperature than charcoal does; while, on the
other hand, the charcoal, when it is kindled, burns more
rapidly, and by its interposition prevents the fusion of the
entire mixture.

There is another detonating composition, of which nitre
is the principal ingredient. It is named *pulvis fulminans*,
or fulminating powder, and is composed of three parts of
nitre, two of subcarbonate of potash, and one of sulphur
triturated together. This detonates when merely heated
without being confined. If 10 grains of it be heated on

an iron spoon, it first fuses, and then explodes with a loud report. Experiments have shewn, that in this experiment the sulphur and potash first combine and form a sulphuret, and accordingly by triturating sulphuret of potash with nitre, a similar compound is formed. By the farther continuance and increase of the heat, a quantity of sulphuretted hydrogen gas is probably produced from the action of the sulphuret on the water present in the mass, and this combining with the oxygen expelled from the nitre, sulphurous acid gas and aqueous vapour are suddenly formed, the expansive force of which is augmented by the heat suddenly extricated. Part of the detonation seems also to be owing to the extrication of the carbonic acid of the carbonate, as, when prepared with potash that has little carbonic acid combined with it, its detonating power is less.

A powder which gives a brilliant white light, and is used in fire works, and for signals, to be seen at a great distance, is composed of 24 parts of nitre, 7 of sulphur, and 2 of realgar, reduced to fine powder.

Nitre is used principally in the formation of gunpowder, and in the preparation of nitric acid. In a small proportion it is sometimes used to preserve animal matter from putrefaction, and it is employed in the processes of pharmacy and in the practice of medicine.

NITRITE OF POTASH.—It has already been stated, that when nitrate of potash is exposed to heat in a retort, a portion of oxygen is expelled from the partial decomposition of the salt; hence the acid was supposed to remain in the state of nitrous acid, and this appeared to be confirmed by the fact that red vapours are disengaged from the residual salt on the affusion of another acid. Berthollet observed, that this nitrite, as it was considered is sensibly alkaline, so as to render the syrup of violet green. This might lead to the conclusion that a part only of the nitric acid is decomposed, and that the remainder, with a portion of nitric

oxide, the latter not contributing to neutralization, exists in the compound, that the salt is therefore not a proper nitric. And Dulong has found, that nitrous acid cannot be brought into direct combination with alkaline bases.

SULPHATE OF POTASH.—This salt is formed by adding sulphuric acid to a solution of potash or subcarbonate of potash, in the proportion producing mutual neutralization. A more economical process, which is generally followed in pharmacy, is to prepare it from the residual mass obtained in the distillation of nitric acid from nitre and sulphuric acid. This is sulphate of potash with an excess of acid. It is dissolved in water; a solution of carbonate of potash is added until the excess of acid is saturated; the liquor by evaporation affords the neutral sulphate of potash. It crystallizes by slow evaporation, its crystals being small and grouped; their figure is that of a six sided prism acuminated by six planes. It is not deliquescent, and scarcely efflorescent; it decrepitates when heated, and at a high heat is melted: 17 parts of water at 60° are requisite for its solution; at 212°, 5 parts are sufficient. Its taste is bitter.

Like the other sulphates, it is decomposed by exposing it to the heat of ignition in mixture with carbonaceous matter, the oxygen of its acid being abstracted, and the sulphur remaining united with the alkali. If iron be mixed with the salt and the charcoal, it attracts much of the sulphur, and allows the alkali to be obtained with less loss; and this process has been proposed as a method of extracting the alkaline base of this salt. Lime has a similar effect with iron, the salt being decomposed, and the alkali obtained by exposing the sulphate to a red heat mixed with charcoal and carbonate of lime *.

A decomposition of this salt, which has engaged the attention of chemists, from being apparently anomalous, is

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* Journal de l'Ecole Polytechnique, Cah. ii, p. 185.

that which it suffers from nitric or muriatic acid. If digested with nitric acid with a moderate heat, a portion of nitrate of potash is formed ; yet sulphuric acid decomposes nitrate of potash, and hence the results appear contradictory ; the nitric acid in the one experiment apparently exerting a stronger attraction to the potash than the sulphuric acid; and in the other, the reverse appearing to be the case. Bergman explained this on the hypothesis that sulphate of potash has an attraction to an excess of sulphuric acid, and that the decomposition (which is always partial) is owing partly to this, and partly to the affinity of sulphuric acid to potash. It now appears that this explanation is just, and that sulphuric acid combines with potash in two proportions. And conformably to the law which regulates such combinations, the quantity of acid in the one salt combined with a given weight of base is double that in the other.

This salt, according to Kirwan, consists of 54.8 of base, and 45.2 of acid. Berard states the proportions at 57.24 and 42.76 ; Berthollet at 58.5 and 41.5 ; Berzelius at 55 and 45 ; and Dr Wollaston assigns those of 54.2 and 45.8.

Sulphate of potash is sometimes employed in medicine. From the alkali it contains, it is used in the manufacture of alum, potash entering into the composition of that salt; and it is employed in some metallurgic operations as a flux. For the two latter purposes, the residuum of the distillation of nitric acid is used, known to the artists by the old name of Sal Enixum.

SUPER-SULPHATE OR BI-SULPHATE OF POTASH, as this salt is named, is formed by exposing the neutral sulphate to heat in a glass vessel with one-third its weight of the acid ; after fusion, and when it has ceased to exhale vapours, it becomes solid, forming a mass of a crystalline texture, and if its solution is slowly evaporated, it affords crystals of a prismatic form. It has a sour taste, and reddens the vegetable colours ; it is more fusible, and more soluble than

the neutral sulphate in water, and is not deliquescent. Considering it as a definite compound in which the quantity of acid is twice that in the neutral sulphate, it consists of 37.2 of base and 62.8 of acid. Berthollet has shewn, at the same time, that by repeated solutions and crystallizations of a super-sulphate of potash, part of the acid is abstracted each time until at length it becomes neutral ; and of course, therefore, that instead of two compounds only, there are intermediate combinations, which can be obtained in a crystalline form, and in which he found by experiment different proportions of acid *.

SULPHITE OF POTASH.—This salt is formed by transmitting sulphurous acid gas through a saturated solution of carbonate of potash in water, until the effervescence from the disengagement of the carbonic acid ceases. Its properties were accurately described by Fourcroy and Vauquelin †. The neutral salt crystallizes in rhomboidal prisms, or in small needles, white and transparent. Its taste is penetrating and sulphureous. Exposed to the air, it slightly effloresces ; it gradually absorbs oxygen, and is converted into sulphate of potash. It is soluble in an equal weight of water at a mean temperature, and in a less quantity of hot water. Exposed to heat, it decrepitates ; at a red heat it is decomposed, sulphurous acid fumes are disengaged, a portion of sulphur is separated, and the alkali remains combined with a quantity of sulphuric acid. It is decomposed by the greater number of the acids, which combine with its base, and expel the sulphurous acid ; nitrous acid converts the sulphurous into sulphuric, by affording oxygen, and nitric oxide gas is disengaged. It is decomposed by barytes and lime, which attract its acid. It consists, according to Dr Thomson's analysis of it, of 54.5 potash, 43.5 sulphurous acid, and 2 water. It was formerly used

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* Mémoires d'Arcueil, t. ii, p. 480.
† Nicholson's Journal, 4to, vol. i, p. 317.

in medicine under the name of Sal Polychrest, as an ape-
, rient, and was prepared by deflagrating equal parts of sul-
phur and nitre, in a crucible heated to redness, though
the product of this process had an intermixture of sulphate
of potash.   It is now discarded from the Pharmacopœias.

PHOSPHATE OF POTASH.— It can scarcely be crystallized,
as by evaporation of its solution, a gelatinous mass is ob-
tained : on its being put aside, however, in a warm place
small prismatic crystals are gradually formed ; its taste is
saline, with a degree of sweetishness.   Exposed to heat, it
becomes liquid, and, after the expulsion of the water, is
fused by a red heat into a glass, which is deliquescent.

PHOSPHITE OF POTASH, formed by saturating phos-
phorous acid with potash, yields, by evaporation, crystals,
which are four-sided prisms bevelled ; its taste is sharp ; it
is very soluble in water.   Heated by the blow-pipe, it swells,
and is melted, with a phosphorescent light.   It is decom-
posed by lime and barytes, and by sulphuric, nitric, and
muriatic acids.   Fourcroy and Vauquelin found it to con-
sist of 49.424 of potash, 39.466 of acid, and 11.11 of wa-
ter.

HYPOPHOSPHITE OF POTASH.—This salt is described
by Dulong as being very soluble in water, and more de-
liquescent even than muriate of lime ; it is also soluble in
alkohol.

BORATE OF POTASH.—This salt is prepared by direct
combination; its properties have been little examined.   It
has a tendency to attract an excess of alkali ; it is soluble
in water; by slow evaporation its solution affords prisma-
tic crystals, which are not changed by exposure to the air.
It is fused into a glass by heat, and is decomposed by lime,
barytes and magnesia.

MURIATE OF POTASH.—When potassium is exposed to
oxymuriatic acid gas, it takes fire and burns with a vivid
red flame ; the product is a saline substance, regarded in
the old theory as dry muriate of potash, according to the

new as chloride of potassium. It is more easily obtained
by neutralizing potash by muriatic acid, and evaporating to
dryness, or by the decomposition of muriate of soda by the
potash of commerce, a process sometimes followed to pro-
cure soda.   Its taste is saline and bitter ; it requires three
parts of cold water for its solution ; boiling water dissolves
half its weight of it, the solution crystallizing on cooling,
though not with regularity.   The form of its crystals ob-
tained by spontaneous evaporation is a cube, and by hasty
evaporation they accumulate by aggregation on the sur-
face of the liquor, so as to form a hollow inverted pyra-
mid.   They are deliquescent in a humid atmosphere. Ex-
posed suddenly to heat, they decrepitate ; by an increase
of heat the salt is fused and volatilized, without decompo-
sition.   According to Kirwan, when dried at the tempera-
ture of 80, the salt consists of 64 of alkali and 36 of acid :
and Berzelius gives the same proportions nearly, 64.19
with 35.81.   Considering it as a chloride, the proportions
conformable to these will be 53 of potassium and 47 of
chlorine. It is little used ; it has sometimes been employ-
ed as a flux in melting some of the metals, to protect them
from the action of the air ; and it serves in the manufac-
ture of alum to afford its alkali, necessary to the constitu-
tion of that salt.

OXYMURIATE OF POTASH.—This salt can evidently be
formed, since oxymuriatic acid gas condensed by a dilute
solution of potash loses its peculiar suffocating odour, and
the alkaline properties are also neutralized, while the li-
quor still retains the power of destroying vegetable colours,
as has been already explained (page 465.) But the com-
pound cannot be obtained insulated or crystallized, as by
concentration of the solution decomposition takes place,
and hyperoxymuriate with muriate of potash are formed.

HYPER-OXYMURIATE OR CHLORATE OF POTASH.—The
process by which this salt is obtained from the transmission

of a current of oxymuriatic acid gas through a solution of
potash, has been already explained, (page 471). The quan-
tity of it deposited by spontaneous crystallization only can
be collected ; for although a portion appears to remain in
solution, it cannot by farther evaporation be obtained free
from the muriate and oxymuriate of potash which are as-
sociated with it.   Vauquelin has found, that it is likewise
formed easily by adding the pure chloric acid to carbonate
of potash ; the carbonic acid is expelled with effervescence,
and if the solutions have been sufficiently strong, and warm,
the chlorate of potash affords a beautiful crystallization in
square plates as it cools *.

Hyper-oxymuriate of potash, obtained by the usual pro-
cess, is in the form of small brilliant scales or thin quad-
rangular plates, white, and of a silvery lustre.   By a slow
spontaneous evaporation, it crystallizes in needle-like crys-
tals.   Its taste is cool and penetrating.   It requires about
17 parts of water at 60° for its solution ; its solubility is so
much increased by heat, that five parts of boiling water
dissolve two parts of it.   It is fused by a moderate heat,
losing a little weight from the escape of water of crystalli-
zation.   By raising the heat nearly to ignition, its acid is
decomposed, and pure oxygen gas is expelled, amounting
to more than one-third of the weight of the salt.   From this
decomposition, and from the quantity of muriatic acid
which remains in combination with the potash, Chenevix
endeavoured to determine its composition : 100 grains of
it, freed from its water of crystallization, yielding 38.3 of
oxygen, and the residuum containing 20 of muriatic acid,
it followed, that its ultimate elements are 38.3 of oxygen,
20 muriatic acid, and 39.2 potash, or, as the two former
constitute the hyper-oxymuriatic acid, it consists of 58.3
of that acid, 39.2 of potash, and 2.5 of water of crystalli-

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* Annales de Chimie, t. xcv, p. 96.

zation.   It has likewise been considered as a ternary com-
pound of chlorine, potassium, and oxygen ; and it may be
regarded as a ternary compound of the radical of muriatic
acid, potassium and oxygen.

Hyper-oxymuriate of potash is not decomposed either
in its concrete state, or in solution in water by light, the
affinity of the base preserving the constitution of the acid.
When subjected to trituration, it appears to undergo some
decomposition, as it gives slight decrepitations, and flashes
of light visible in the dark.

It is decomposed by the acids, decompositions which
were examined by Hoyle, and afterwards by Chenevix. If
a few grains be thrown into concentrated sulphuric acid,
small explosions or decrepitations take place, accompanied
sometimes with flashes of light ; the liquor around the salt
acquires an orange or red colour; and a dense yellow va-
pour, having an oppressive smell, floats above.   This is
hyper-oxymuriatic acid, mixed with oxymuriatic and eu-
chlorine gases.   If heat be applied, an explosion with a
vivid flash takes place, as Chenevix found, when the li-
quid has attained the temperature of 125°, and accidents
have repeatedly happened from making this experiment.
The explosion even happens when the acid is a little di-
luted with water.   If it is more diluted, a wide-necked re-
tort being used, and the heat cautiously applied, the action
is more moderate ; the hyper-oxymuriatic acid is decom-
posed, and appears to be converted principally into mu-
riatic acid and oxygen ; and by other modes of promoting
the mutual action, euchlorine gas, and the gas which con-
tains a still larger proportion of oxygen are obtained, as
has been already explained.

The action of nitric acid on hyper-oxymuriate of potash
is similar to that of sulphuric acid, but less violent.

Muriatic acid is converted into oxymuriatic acid, by re-
ceiving the excess of oxygen of the hyper-oxymuriatic acid.

A few grains of the salt, added to an ounce of muriatic acid, give it the property of destroying the vegetable colours.

When inflammable substances are presented to hyper-oxymuriatic acid disengaged from its combination by sulphuric or nitric acid, it acts on them with energy; brilliant combustions are exhibited, and the experiments can be made with safety only on small quantities of the materials. If five or six grains of the salt be mixed with two or three grains of sugar, and be thrown into sulphuric acid, or touched with it, there is a vivid combustion; or if the salt in powder be made into a soft paste with any essential or fixed oil, it is inflamed in a similar manner. The same phenomena are exhibited with camphor, resins, charcoal, sulphur, and other inflammables. The experiment may even be managed so as to cause some of them to burn under water. With nitric acid the effects are similar.

The action of hyper-oxymuriate of potash on inflammable substances, when promoted by trituration or percussion, is extremely violent. A number of experiments of this kind were made by Fourcroy and Vauquelin, and by Hoyle, who have given the proportions to be used, and their effects *. A grain of the salt with half a grain of sulphur rubbed in a stone mortar decrepitates strongly, or if struck on an anvil gives a loud report with a flash of light. Two grains with one of charcoal give a strong flame. Half a grain of phosphorus, covered with the same quantity of the salt, and struck, gives a report extremely loud, and small particles of the phosphorus are projected with violence, so as to render the experiment somewhat dangerous, at least if any larger quantities than these be used. Antimony, arsenic, zinc, and a number of metallic sulphurets, fulminate when their mixture with the

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Nicholson's Journal, 4to, vol. i, p. 168; and vol. ii, p. 294.

salt is struck with a smart blow; and similar phenomena
are produced by many inflammable substances, both solid
and liquid. These mixtures are likewise inflamed by the
electric spark, and by the application of heat. Some of
them, that for example of the salt with arsenic, inflame
with such violence as to render the experiment dangerous.

These phenomena arise from the rapid combination of
the oxygen of the hyper-oxymuriatic acid with the inflam-
mable body, and the instantaneous formation of a product,
elastic, and having its elasticity augmented, by the large
quantity of caloric set free by the new combination.
What confirms this explanation is, that of the metals,
those only detonate when struck with the salt which are
volatile. The effect of the mechanical compression is to
be ascribed to its suddenly approximating the particles of
oxygen and of the inflammable matter, and perhaps fa-
vouring their union by the slight momentary elevation of
temperature which it must produce. This is the general
theory of detonations from percussion, and the violence of
those produced with the hyper-oxymuriates arises from
the large quantity of oxygen in their composition, and the
weak affinity by which it is retained.

From this property of the hyper-oxymuriate of potash
it was an obvious idea, that it might be employed for the
preparation of a powerful gunpowder. The experiment
made under the direction of Lavoisier at Essone in 1788
must preclude such a trial, the materials having exploded
during the trituration, and two individuals having lost
their lives. Mixtures of this salt with an inflammable sub-
stance have even been known to explode spontaneously, or
from a very slight agitation.

It is usually from this salt that oxygen gas is procured,
where it is of importance to have it perfectly pure.

FLUATE OF POTASH.—Fluoric acid combines with po-
tash with much heat; the salt formed has a sharp taste,

crystallizes with difficulty, is very deliquescent, and very soluble in water. Sulphuric acid decomposes it in the cold, with a brisk effervescence from the disengagement of fluoric acid in vapour.

SILICEO-FLUATE OF POTASH.—The salt formed by saturating the liquid siliceo-fluoric acid with potash, has been described as very soluble in water, so that its solution may be evaporated to the consistence of a jelly without crystallization. According to Gay-Lussac and Thenard, however, when to the liquid superfluate of silex, potash is added, a compound is formed slightly acid, so sparingly soluble as to require six or seven hundred parts of water for its solution, and the filtrated liquor scarcely affords any residuum on distillation. This triple salt forms a transparent jelly, but becomes pulverulent from a moderate heat; at a red heat the acid holding silex dissolved is expelled. It is decomposed with effervescence by sulphuric acid. It acts on glass when aided by heat.

HYDRIODATE OF POTASH.—This salt, formed by saturating hydriodic acid by potash, is very soluble in water, 100 of water at 65° dissolving 143 parts; in crystallizing it, and still more on drying it or fusing it, Gay-Lussac considers it as suffering decomposition, the hydrogen of the acid uniting with the oxygen of the potash, and the iodine with the potassium : this, however, is only a hypothetical inference : the solid compound is obtained in a crystalline form; it is composed, according to Gay-Lussac's view, of 100 of iodine with 31.34 of potassium ; the hydriodate of potash undecomposed is composed of 100 of hydriodic acid with 37.43 of potash.

OXIODATE OF POTASH is obtained in small crystals of a cubic form, which are not altered from exposure to the air ; 100 parts of water at 60 dissolve 7.5 of the salt. It deflagrates on burning fuel. It is decomposed by heat, requiring for this a temperature somewhat higher than

oxymuriate of potash, gives out oxygen, and what Gay-Lussac considers as ioduret of potassium remains. Its composition is represented by 22.6 of oxygen, and 77.4 of ioduret of potassium, composed of 58.9 of iodine and 18.5 of potassium.

Potash, from the numerous combinations of which it is susceptible, is an important chemical agent, and is hence applied to many purposes in the arts, as in bleaching, in the manufacture of soap, of glass, &c. applications afterwards to be noticed. It is used in a number of the processes of pharmacy, and it is employed in medicine as an antacid and lithontriptic.

Besides existing in vegetables, it is a principle in several of the animal fluids. It has also been discovered in the mineral kingdom as a constituent part of several fossils. Klaproth discovered it first in the leucite. Vauquelin found it in the lava in which that fossil is imbedded; Dr Kennedy detected it in pumice, and it has since been discovered in stones which cannot be suspected of volcanic origin, as in zeolite, feldspar, lepidolite, and others. Some of these contain 16 or 18 of potash in 100 parts.

CHAP. III.

OF SODA.

Soda, the third of the alkalis, has been named Mineral or Fossil Alkali, as it is more abundant than the others in the mineral kingdom, and was even supposed exclusively to exist in it. There is reason to believe that it is the natron or nitrum of the ancients. Du Hamel first shew-

ed that it is a substance different from potash *; and
Margraaf added to the facts from which this conclusion
was deduced, and established some of its characteristic
properties.

The nature of this alkali, previous to the discoveries of
Davy, was equally unknown with that of potash. The
same analogy had led to the conclusion, that it is a com-
pound; and similar conjectures had been formed as to its
composition; magnesia having been supposed to be its
base, and nitrogen or hydrogen its alkaline principle. Sir
H. Davy having effected the decomposition of potash,
submitted soda to the same modes of analysis, and obtain-
ed similar results. On placing it in the galvanic circuit,
in the mode already described with regard to potash, glo-
bules of a metallic appearance were produced at the nega-
tive surface, which often burnt at the moment of their for-
mation, and sometimes exploded with violence, separating
into smaller globules, which darted through the air in a
state of vivid combustion. An aëriform fluid was disen-
gaged at the positive surface, which proved to be pure
oxygen. To effect this decomposition, a greater intensity
of galvanic action was required than was necessary to de-
compose potash.

The reproduction of soda from this substance was simi-
lar to that of potash from the base of that alkali. When
the base of soda was exposed to the air, a crust of alkali
formed on its surface, and oxygen was absorbed. When
heated confined in a portion of oxygen gas, a rapid com-
bustion with a brilliant white flame took place, and soda
was produced in the state of a solid white mass.

To the substance thus procured from soda he gave the
name of Sodium.

Regarding soda as a compound of this inflammable me-
tallic matter and oxygen, he endeavoured to determine the

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* Mémoires de l'Acad. des Sciences, 1736.

proportions in which they combine to form it. From the results of the combustion of the base of soda in oxygen gas, he inferred that 100 parts of soda consist of 80 of base and 20 of oxygen. From the results of its oxidation by the decomposition of water, the proportions were estimated to be 77 of base and 23 of oxygen. The mean proportions of these two modes are 78.5 and 21.5. The results of more accurate subsequent experiments on the combination of sodium with oxygen gave as the proportions 74.4 and 25.4, or 100 with 34.14. The proportions inferred by Gay-Lussac and Thenard from the results of the conversion of sodium into soda by oxygenation by the agency of water differ little from these, being 74.63 of sodium, and 25.37 of oxygen; or 100 with 34 *; and those assigned by Berzelius agree very nearly, being 100 with 34.52 †.

The process of Gay-Lussac and Thenard, by which potassium is obtained from potash by the medium of iron, may be applied to obtaining sodium from soda, employing the same apparatus, and observing the same precautions; it is in particular necessary to have the soda free from potash, as otherwise the alloy of potassium materially modifies its properties. A higher heat is necessary than in the process for procuring potassium, and therefore the soda should be passed very slowly over the iron. The greater difficulty of obtaining sodium than potassium by this process, Davy supposes owing to the former having less affinity than the latter to hydrogen, and being less abundantly dissolved by it, the hydrogen probably contributing by its affinity to potassium to its production and volatilization. Gay-Lussac and Thenard found, that sodium might be produced by the action of iron from its subcarbonate, but a part only of the subcarbonate of soda could be decom-

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* Recherches Physico-Chimiques, t. i, p. 121.
  Annals of Philosophy, vol. iii, p. 360.

posed, whatever degree of heat was applied : this they sup-
posed to arise from the subcarbonate not containing so
much water as the common soda does, and hydrogen being
therefore not afforded to favour the volatilization of the
sodium.   They introduced a current of hydrogen gas,
when the sodium had ceased to be produced, and imme-
diately the production of it took place.   By a farther ex-
periment they proved that this does not depend on any
pecular affinity exerted by hydrogen, for the introduction
of nitrogen had the same effect : the operation therefore
depends on the principle already stated, that a current of
aërial fluid promotes the transition of a more fixed body
into vapour *.

The process of Curaudau, in which charcoal is employ-
ed, described under the history of potash, likewise suc-
ceeds with soda ; but the quantity of sodium obtained is
very small.

The easiest process for procuring sodium is the heating
ignited muriate of soda with potassium : at a red heat so-
dium is obtained ; no hydrogen is disengaged : two parts
of potassium produce rather more than one of sodium †.

Sodium is regarded as the real metallic base of soda. If
potassium, however, contain hydrogen, it is not improbable
that sodium may retain a portion of the same element.

It remains to state the properties of Sodium.

SODIUM is white, opaque, and when examined under a
film of naphtha has the lustre and appearance of silver. It
is exceedingly malleable, and much softer than any com-
mon metallic substance, being nearly of the consistence of
wax.   When pressed upon, with a small force, it spreads
into thin leaves, and this property does not diminish when
it is cooled to 32° Fahrenheit. It conducts electricity and
heat in a similar manner to potassium.

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* Recherches Physico-Chimiques, tom. ii, p. 240.
† Davy, Philosophical Transactions, 1811.

Its specific gravity is less than that of water.   It swims in oil of sassafras of 1.096, water being one, and sinks in naphtha of specific gravity .861.   By mixing oil of sassafras and naphtha, until a fluid was formed in which the globule of sodium remained at rest above or below, Mr Davy found its specific gravity to be to that of water as .9348 to 1.   Gay-Lussac and Thenard state it rather higher—at .97223.

Sodium has a higher point of fusion than potassium ; it begins to lose cohesion at about 120°, and is a perfect fluid at about 180° ; according to Gay-Lussac and Thenard its point of fusion is 194°. It is also less volatile ; it remains fixed in a state of ignition at the point of fusion of plate glass.

When sodium is exposed to the atmosphere, it tarnishes, and by degrees becomes covered with a white crust, which deliquesces more slowly than the substance which forms on potassium.   This crust is pure soda.

Sodium is less inflammable than potassium ; it combines with oxygen slowly, and without any luminous appearance, at common temperatures ; and when heated, though the combination becomes more rapid, no light is emitted till it has acquired a temperature nearly that of ignition ; it then burns with a light similar to that from charcoal, but brighter : the flame it produces in oxygen gas is white, and it sends forth bright sparks. One grain of sodium absorbs very nearly a cubic inch of oxygen gas.

Sodium like potassium combines with different proportions of oxygen ; and the results, as Gay-Lussac and Thenard have shewn, are similar. The product of its combustion in oxygen gas, or even in atmospheric air at a high temperature, is not the alkali, but an oxide containing one half more oxygen than that which enters into the composition of the former.   The proportions are 100 of sodium and 51 of oxygen.   This oxide of sodium at the maximum is of a dull greenish-yellow, or brown colour, if the so-

dium has been burnt on platina. It is fusible, but much less so than common soda, requiring a high red heat for its fusion; it is decomposed by water, oxygen gas being disengaged, and soda formed which remains in solution; it also yields a portion of its oxygen to inflammable bodies when heated with them, and returns to the state of soda; and there is a similar result when it is heated in acid gases. This oxide is also formed by exposing soda to a red heat in contact with the air. The oxide which constitutes soda is formed by the agency of water; either by its direct action on sodium, or by its action either on the oxide at the maximum or at the minimum, oxygen being disengaged from the former, and hydrogen being disengaged in consequence of the decomposition of the water by the latter. The oxide which is at the lowest degree of oxidation is obtained by the same process as that by which the corresponding oxide of potassium is formed; it is of a greyish-white colour, without metallic lustre, is brittle, and affords hydrogen with water, attracting oxygen from the water and passing into soda *.

When sodium is thrown upon water, it produces effervescence, with a hissing noise, and forms soda, which is dissolved; while hydrogen gas is disengaged. It gives no luminous appearance; but when thrown into hot water, the decomposition is more violent, and a few scintillations are observed at the surface of the fluid, owing to particles of the base, which are thrown out of the water, sufficiently heated to burn in passing through the atmosphere.— And when a globule is brought in contact with a drop of water, or with moistened paper, the heat produced (there being no medium to carry it off rapidly) is usually sufficient to kindle the sodium. When placed in contact with water and with some gases, as sulphurous acid, nitrous

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* Recherches Physico-Chimiques, tom. i, p. 150.

oxide, and oxymuriatic acid gases, it is also inflamed.—
When thrown upon nitrous acid, a vivid inflammation is
produced ; with muriatic and sulphuric acids, much heat
is generated, but no light.   When plunged beneath the
surface of the acids, it is rapidly oxygenated ; soda is pro-
duced, and combines with the acid.   Heated in carbonic
acid it decomposes it, attracting oxygen, but without in-
flammation ; it burns in sulphurous acid gas, and in mu-
riatic acid gas there is a weak light produced, and hydro-
gen gas is disengaged.   It also burns vividly when heated
in nitrous oxide gas, and in oxymuriatic acid gas.

Sodium, when heated in hydrogen gas, does not appear
to be dissolved ; and as the gas disengaged in the oxida-
tion of it in cold water does not inflame, it seems not to
be capable of combining even with nascent hydrogen. At
a high degree of heat, however, the combination is esta-
blished, Gay-Lussac and Thenard having found, that hy-
drogen gas passed through the tube in which soda is de-
composing by the agency of iron, on escaping into the air
suffered spontaneous combustion with a white flame.

There is scarcely any difference in the phenomena of
the agencies of the base of soda, and that of potash on sul-
phur and phosphorus.   It combines with sulphur in close
vessels filled with the vapour of naphtha with great vivid-
ness, with light, heat, and often with explosion from the
vaporization of a portion of sulphur, and the disengage-
ment of sulphuretted hydrogen gas. The sulphuretted so-
dium is of a deep grey colour.   The combination with
phosphorus is attended with less illumination.   The phos-
phuret has the appearance of lead, and forms phosphate
of soda by exposure to air, or by combustion.   Sodium
likewise decomposes sulphuretted and phosphuretted hy-
drogen ; with the aid of a moderate heat, hydrogen is e-
volved, and sulphuret or phosphuret of sodium formed.

Sodium combines with the metals.   In the quantity of
$\frac{1}{40}$ it renders mercury a fixed solid of the colour of silver,

and the combination is attended with a degree of heat. It makes an alloy with tin, without changing its colour ; it acts upon lead and gold when heated, and, as Gay-Lussac and Thenard have shewn, combines with a number of other metals. In its state of alloy it is soon converted into soda by exposure to air, or by the action of water. The amalgam of mercury and sodium seems to form triple compounds with other metals.

The combination of sodium with potassium presents results of some interest. Davy, by exposing mixtures of potash and soda to the action of ignited iron, obtained alloys of the two alkaline bases : these, whether the potassium or the sodium were in excess, were fluid at common temperatures ; and the compound, with an excess of potassium, was even lighter than potassium itself. When a globule of the fluid alloy is touched by a globule of mercury, they combine with an evolution of heat, and form when cold a solid so hard as not to be cut by a knife [*]. These alloys have also been examined by Gay-Lussac and Thenard : they formed them by direct combination of the potassium and sodium in different proportions, and found that an alloy was formed always more fusible than sodium, and frequently more fusible than potassium. Three parts of sodium and one part of potassium form one fusible at zero, and which, when its temperature is reduced by a mixture of snow and salt, crystallizes and becomes brittle : if the proportion of sodium is increased, the fusibility is less, but still is greater than that of the sodium itself. If the proportion of potassium is increased, alloys are formed more and more fusible, and the fusibility of which does not diminish but when the quantity of potassium is very large : that from ten parts of potassium and one of sodium is liquid at zero, and has the remarkable property of being lighter than rectified naphtha. These chemists assign this as the cause

* Philosophical Transactions 1809.

that the fusibility both of potassium and sodium have been stated by some chemists to be lower than they actually are; the alkalis employed in their preparation having often an intermixture of each other, whence an alloy is formed *.

Sodium like potassium abstracts oxygen from the greater number of metallic oxides and metallic salts, but requires rather a higher temperature than potassium does to promote its action.   It presents similar results in its action on ammonia, absorbing the ammoniacal gas when heated in it, while hydrogen is evolved, and the sodium is changed into a substance of an olive green colour, which has properties and chemical relations similar to the substance formed by the action of potassium on ammonia.

SODA.   After the account of the base of this alkali, I have to deliver the chemical history of the alkali itself.

Soda exists in the mineral kingdom in various states of combination, from some of which, particularly from the muriate, it may be extracted; and the native carbonate has been introduced into the arts, for purposes dependent on the agency of its alkali.   It is generally obtained, however, from the combustion of marine vegetables.   In different countries, different plants are burned for this purpose.   In the north of Scotland the different kinds of sea-weed are employed, and furnish an impure alkali named Kelp.   The sea-weeds being dried, are burnt in pits dug in the sand, or on the surface surrounded with loose stone; fresh quantities being added, and the whole being frequently stirred until it become semi-fluid; this when cold forms hard masses †.   In France and Spain the salsola, salicornia, and several others, are cultivated to afford the alkali.   The plants are collected when in maturity, and are dried by exposure to the sun; they are put into heaps in pits, and

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* Recherches Physico-Chimiques, tom. i, p. 110.
† Jameson's Mineralogy of the Scottish Isles, vol. ii, p. 245.

burned slowly * ; the saline matter thus obtained is nam-
ed Barilla. The following is the outline of the process as
it is conducted at Alicant. The plants cultivated for the
purpose, the *salsola sativa*, and *salsola soda*, are pulled up
in autumn and left to dry in heaps. When dried they are
burnt. " Spherical holes, capable of containing about
thirty hundred weight of soda, are made in the earth ; above
each cavity are placed two bars of iron, which support the
plants to be burnt, and which are mixed with reeds or straw.
Care is taken to make choice of a day when the wind is
not too strong, otherwise the soda would burn too rapidly,
and be reduced with difficulty to a solid mass ; it is neces-
sary also that the air should not be entirely calm ; for in
that case the smoke, by not being carried off, stains the
soda. The barilla in burning experiences a kind of fusion,
and is reduced to a red mass, which is stirred once or twice,
in order that the fusion should be more complete. When
the pits are full, which generally requires a whole night,
the matter is covered with earth, and it is suffered to cool
for ten or twelve days ; the cake formed is then uncover-
ed †."

The saline matter from the combustion of sea-plants is
of a black or bluish colour, from the presence of charcoal
and oxide of iron ; it is in masses which are hard and of
a heterogeneous texture, and when perfectly dry is often
covered with a white efflorescence of carbonate of soda.
Barilla has been analysed by Mr Kirwan. He gives the
products from one pound of the best quality in the follow-
ing proportions : Carbonic acid, 960 grains ; charcoal,
861.8 ; lime, 542.8 ; magnesia, 127 ; argil, 131.2 ; silex,
249.5 ; SODA PURE, 842 ; SODA IMPURE, 250 ; SODA mixed
with common salt, 127 ; sulphate of soda 125 ; muriate

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* Annales de Chimie, t. xlix, p. 275.
† Philosophical Magazine, vol. xiii, p. 89.

of soda 70; earth deposited, 20 *.   Chaptal in different
varieties of it, found the proportion of carbonate of soda
to vary from less than 1 to 7 oz. in one lb. with muriate of
soda, sulphate of potash, and sulphate of magnesia †.   Mr
Jameson found, that, while the barilla of Alicant contained
in 100 lbs. 23½ of alkali, the quantity in the kelp of Scot-
land was not more than from 2½ to 5lbs. ‡.

The origin of the soda afforded by the combustion of
these plants is not well ascertained.   It may pre-exist in
the vegetable, and this appeared to be established by Vau-
quelin's analysis of the principal plant that affords it, the
salsola.   Its infusion in cold water afforded by evapora-
tion two salts, having soda for their base, muriate and
carbonate of soda, and the residuum of its distillation in
close vessels gave similar salts; combustion, therefore,
Vauquelin concludes, serves merely to develope the saline
matter in the plant, by consuming its other principles ‖.

It has also been supposed, however, that the soda may
exist in the plant under the form of muriate of soda, de-
rived from the sea-water; that the plant may, in common
with others, afford potash by combustion, which will de-
compose the muriate of soda, the soda of which receiving
carbonic acid from the burning of the charcoal, carbonate
of soda is formed.   To this supposition, the results of
Vauquelin's analyses are so far unfavourable, as they shew
that a portion of carbonate of soda exists in the vege-
table.   They prove also, however, that it contains muriate
of soda; and it is possible, that by the combustion the
quantity of carbonate of soda may be increased by a de-
composition of part of this.   That the muriate is not en-
tirely decomposed, is evident from a quantity of it being
always found in barilla.

* Transactions of the Iris Academy, 1789, p. 12.
† Annales de Chimie, tom. xlix, p. 279.
‡ Mineralogy of the Scottish Isles, vol. ii, p. 248.
‖ Annales de Chimie, tom. xviii, p. 65.

That marine vegetables derive the soda they afford from their situation, conveying to them muriate of soda, which is decomposed by the process of vegetation, appears to be proved by experiment. Du Hamel planted sea plants in an inland situation, burnt them, and collected the ashes, continuing the experiment for a number of years : Cadet, examining the saline matter afforded from these ashes, found, that, in the quantity which had been produced the first year, soda predominated ; in the succeeding years, the production of potash had augmented rapidly, and at length it alone was produced *.

The soda is abstracted from barilla, by lixiviation with boiling water. The solution is filtrated, and evaporated ; it affords crystals, which consist of soda combined with carbonic acid, from 3 to 5 ounces of this crystallized carbonate being procured from 1 lb. of barilla.

To obtain pure soda, carbonate of soda is to be mixed with an equal weight of quicklime, which being slaked by the addition of a little water, as much water is to be added as will bring the whole to a thin consistence. The mixture is put into a funnel, the neck of which is obstructed with a piece of linen, and water added as the filtration proceeds, until 5 or 6 times the weight of the carbonate of soda used has passed through. The lime attracts the carbonic acid, and the soda is dissolved by the water. Though purer than the potash obtained by a similar process from carbonate of potash, it is not of perfect purity, and to obtain it in this state, the process of Berthollet must be followed ; the solution of soda being evaporated to the consistence of honey, alkohol being added, and the other steps followed already described in the history of potash. Berthollet has remarked, that this process does not answer so well with soda, the separation of the solution in alkohol

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* Mémoires de l'Acad. des Sciences, 1782, p. 146.

into two portions, one holding the pure soda, the other
the carbonate of soda and other salts in solution, taking
place only towards the end of the evaporation; and even
then it does not appear to be complete.

Soda thus purified is in a solid white mass, which fuses
at a heat inferior to redness; it is capable of crystalliza-
tion, though with difficulty, from its solution in water or
alkohol; the form of its crystals is prismatic, but not very
regular. In its crystallized state, it contains a portion of
water; but when kept in fusion for some time, this water
was supposed to be dissipated, and the fused soda was re-
garded as the real alkali. The observations and experi-
ments, however, which proved the existence of water in
fused potash, have proved its existence in fused soda.
D'Arcet, from the results of the experiments stated under
the history of potash, inferred that soda in this state con-
tains 0.28 of combined water. Berard, by a different
mode of investigation, fixed the quantity at 18.86, or, cor-
recting the results of D'Arcet's method, at 20 *per cent.*
Davy, from the loss of weight which ignited soda mixed
with boracic acid sustained from exposure to heat, con-
cluded that it amounts to 23 or even 25. And Gay-Lus-
sac and Thenard, as the mean from several modes of de-
termining it, state it at 25. This combined water appears
to be retained with as much force as the combined water
in potash.

It also modifies the properties of the alkali, in a similar
manner as it does those of potash; soda formed from the
oxygenation of sodium, so as to be free from this water,
being of a grey colour, harder, heavier, and less fusible,
than ignited soda, prepared by the medium of alkohol *.
It instantly combines with water, producing heat, and form-
ing the white hydrate of soda. According to the view I

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* Davy, Philosophical Transactions, 1811.

have illustrated, this hydrate is not to be regarded as a compound of what is called real soda and water; it contains the elements of water, and is a ternary compound of sodium, oxygen and hydrogen. The chemical agencies of the substance which might be regarded as real soda formed from the combination of sodium with oxygen, cannot be determined, as it can scarcely be submitted to any trial without the presence of water, which converts it immediately into common soda.

Soda like potash is extremely acrid and caustic; has a strong attraction to water, so as to imbibe it from the air, but is not so powerfully deliquescent, and indeed in a dry atmosphere scarcely becomes humid. It requires, too, rather a larger quantity for its solution, though it is still abundantly soluble. It changes the vegetable colours to a green, is powerful in neutralizing the acids, and unites with oils forming a hard soap.

Soda like potash combines with oxygen, when exposed at a red heat to the air, and passes to the state of the oxide of sodium at the maximum of oxidation, parting probably at the same time with its portion of water.

It acts in a similar manner on inflammable bodies, dissolving apparently a small portion of charcoal, so as to become coloured, and combining with phosphorus, and at the same time enabling it to decompose water if present, and form phosphuretted hydrogen. Its action on sulphur too is similar; they combine by fusion, forming a solid sulphuret; and in the humid way, they by mutual action decompose water, and form a sulphuretted hydro-sulphuret, analogous to that of potash. With sulphuretted hydrogen it forms a saline compound, the properties of which were described by Vauquelin *. It is of a white colour, transparent; crystallized in tetraedral prisms acuminated by four planes. Its taste is acrid and alkaline, soon becom-

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Annales de Chimie, tom. xli, p. 150.

ing bitter. It dissolves abundantly in water, and produces cold in dissolving. Its solution is colourless, but gives a green tinge to paper : It has a smell of sulphuretted hydrogen. Acids produce with it a brisk effervescence, and render this odour very strong ; but they do not render the liquid turbid. The nitrous and oxymuriatic acids, however, have this effect, and produce a precipitate of sulphur,— owing to their decomposing the sulphuretted hydrogen, by affording oxygen to its hydrogen, while the other acids merely expel it. This salt precipitates all the metallic oxides from their solutions. It does not precipitate the earths, with the exception of alumina, zircon, and ittria. It may be distinguished from the hydro-sulphuret of potash, which is similar in properties, by adding a few drops of the solution of alumina in sulphuric acid ; the hydro-sulphuret of potash gives rise immediately to a crystallization of alum ; while that of soda has no such effect.

The action of soda on the metals is scarcely so energetic as that of potash, nor does it appear to combine so readily with the metallic oxides.

Its action, too, on the earths in the humid way is rather feeble, and indeed it scarcely dissolves any of them except silica. It combines with them, however, by fusion, and vitrifies with them even more readily perhaps than potash. With silica it forms a very perfect glass, and when the alkali is in larger proportion, forms another compound soluble in water.

Soda combines with all the acids, and in power of neutrallization rather exceeds potash. Its salts are all soluble and crystallizable. They are in general distinguished by their crystalline forms, as there is no striking generic character by which they can be recognised. They are discriminated from the salts of potash, to which they bear the greatest resemblance, by the negative qualities of not yielding crystals of alum, when added to a solution of sulphate of alumina, not affording a deposite of a supertar-

trate from tartaric acid, and not throwing down any pre-
cipitate from muriate of platina.

CARBONATE OF SODA.—Soda like potash combines with
carbonic acid in two proportions, forming salts, in one of
which the quantity of carbonic acid is double that in the
other.   The one is a Subcarbonate, and the other is dis-
tinguished by the name of Bi-carbonate.

Subcarbonate of soda is obtained from the incineration
of marine plants, and differs from the subcarbonate of po-
tash in assuming easily a crystallized form.   It is procur-
ed from the purer kinds of barilla lixiviated with water, the
clear solution being poured off and evaporated, until on
cooling it affords crystals.   It is also found native in India,
Egypt, and Syria, in the form of crystalline masses, or of
an efflorescence, and in solution in lakes in Hungary and in
Egypt.   It crystallizes in ochohedrons, composed of two
four-sided pyramids with rhomboidal bases joined, and al-
so in rhomboidal tables. Its taste is alkaline, and it changes
to a green the vegetable colours.   It is efflorescent, so as
in a dry atmosphere to be soon reduced to a powder.   It
requires, at a medium temperature, twice its weight of wa-
ter for its solution, and rather less than its own weight of
boiling water, its saturated solution crystallizing on cooling.
Exposed to heat, it suffers the watery fusion from the large
quantity of water of crystallization which it contains; as
this is dissipated, it appears as a dry white powder, which
by an increase of heat may be fused and partially decom-
posed.   The proportions of its constituent principles are
stated by Kirwan at 21.58 of soda, 14.42 acid, and 64 wa-
ter of crystallization, with which the estimate of Bergman
almost precisely agrees: that of Berard's differs little, being
23.33 of soda, 13.98 of acid and 62.69 of water.   The salt
freed from its water of crystallization consists according to
Berard of 62.5 of soda and 37.5 of acid, according to Kir-
wan and Dulong of 60 and 40.

This salt suffers decompositions similar to the carbonate
of potash from lime, barytes, and strontites, and from the
acids.   It is applied nearly to the same uses.   It is even
preferred in the manufacture of glass, and in soap-making
it affords a soap which becomes concrete, while that from
potash remains soft.   In these arts, it is used under the
form of barilla, and what in this country is named kelp,
which is obtained by burning the different varieties of sea-
weed.   A purer carbonate of soda has also been introduced
into the market, obtained by various processes to be after-
wards described, from the decomposition of sea-salt, of
which soda is the base.

BI-CARBONATE OF SODA.—This salt is formed on ex-
posing a solution of the subcarbonate to an atmosphere of
carbonic acid gas, or transmitting a current of the gas
through the liquor ; it is also formed by exposing the sub-
carbonate to heat in a state of saturated solution, with about
a sixth of its weight of subcarbonate of ammonia. The liquor
deposites an aggregation of crystalline plates, but by a slow
evaporation of a less concentrated solution, more regular
crystals are formed.   The taste of this salt is milder than
that of the subcarbonate, but is still sensibly alkaline, and
it changes the vegetable blues to a green ; it is decompos-
ed by a low red heat, and loses half its quantity of car-
bonic acid, passing to the state of subcarbonate.   Dr Wol-
laston, by whom this relation in the proportion of the two
salts was first observed, assigns as the proportions in the
one, 100 of soda with 70.6 of carbonic acid, and in the other
100 with 141.2.   The crystallized bi-carbonate consists, ac-
cording to his scale, of 37.1 of soda, 52.2 of acid, and 10.7
of water.   Other analyses have stated the proportion of wa-
ter so high as 14, 20, or 23 *per cent*.

Soda supersaturated with carbonic acid in a state of
solution is medicinally employed as an antacid and lithon-
triptic, and is even more employed than the supercarbonate
of potash, on the supposition that it is more mild.

NITRATE OF SODA.—With soda nitric acid forms a neutral salt, which crystallizes in rhomboidal prisms, hence formerly named rhomboidal or cubic nitre. It is not found in nature, but is formed easily by the combination of the acid and alkali. Its taste is cool, penetrating, and somewhat bitter; it slightly attracts moisture from the air; it is soluble in about 3 parts of water at the temperature of 60, and in an equal weight of boiling water, though some have represented it as being scarcely more soluble in hot than in cold water; it is scarcely so fusible as the nitrate of potash, but is otherwise decomposed by heat in the same manner. It consists, according to Kirwan, of 53.21 of real acid, 40.58 of alkali, and 6.21 of water of composition. It acts upon inflammables in the same manner that nitrate of potash does; when deflagrated with charcoal in a proper proportion, its acid is destroyed, and the alkali remains combined with carbonic acid, which affords one of the easiest methods of obtaining soda. As it contains more oxygen than common nitre does, it has been imagined that it would form a more powerful gunpowder. It is affirmed, however, by Vauquelin, that the gunpowder into which it enters is less powerful; and were it even more so, it would not be preferable, as it is more apt to attract humidity on keeping.

Nitrate of soda, like that of potash, is decomposed by sulphuric acid, by clay and siliceous earth, affording nitric acid by distillation. It is likewise decomposed by potash, which shares its acid with the soda. It is not applied to any useful purpose.

SULPHATE OF SODA.—Glauber, a German alchemist, examining the residuum of the distillation of muriate of soda by sulphuric acid, discovered this salt, which hence derived from him the name by which it is commonly known. Having been largely employed in medical practice, it is prepared by various processes on a large scale. One is that pointed out by Glauber,—the distillation of muriatic acid; the

saline mass which forms the residuum consists of the soda
of the muriate of soda, with sulphuric acid in excess.   It
is dissolved in water ; the excess of acid is neutralized by
adding lime ; the liquor is drawn off into shallow leaden
vessels, and on cooling affords the sulphate in crystals.   It
is also obtained in the manufacture of sal ammoniac, or
muriate of ammonia, being formed in combining the mu-
riatic acid of muriate of soda with the ammonia, and be-
ing purified by dissolving the mass in water, and adding a
little lime to disengage any ammonia that may remain.
This salt also exists native in mineral springs.   It some-
times effloresces on the walls of old buildings.   The figure
of its crystals is a six-sided prism bevelled at the extremi-
ties.   Its taste is strongly saline and bitter.   It is efflores-
cent ; exposed to a dry atmosphere, the surface of the cry-
stals becomes white and opaque, and at length they fall in-
to powder.   It is soluble in rather less than three parts of
water at 60° ; and in less than its own weight at 212°.
Exposed to heat it undergoes the watery fusion ;   the wa-
ter of crystallization is dissipated ; and by a strong red heat
it may be melted.

Sulphate of soda suffers decompositions similar to those
of sulphate of potash.   Barytes and strontites abstract its
acid ; potash does so partially ; nitric and muriatic acids
digested upon it share its base with the sulphuric acid.
Heated with carbonaceous matter, its acid is decomposed ;
and this process is sometimes followed in the arts to pro-
cure soda, lime or iron being added to combine with the
sulphur of the acid.   According to Kirwan, the crystallized
sulphate consists of 18.48 of soda, 23.52 of acid, and 58
of water, with which the proportions given by Berzelius
very nearly correspond.   When its water of crystallization
is expelled by a heat of 700°, it consists of 44 of soda and
56 of acid : this proportion is also given by Dr Wollaston.
Berard states it at 47.22 of base and 52.78 of acid.

SULPHITE OF SODA may be prepared by saturating a

solution of soda with sulphurous acid. It is white and transparent, its taste is cool and somewhat sulphureous, its crystals are prismatic; they effloresce on exposure to the air, and the acid is converted into sulphuric, by absorbing oxygen. Exposed to heat, it undergoes the watery fusion, and is then decomposed. It is soluble in 4 parts of water; it requires less warm water, and the latter solution crystallizes on cooling. It consists, in the crystallized state, according to Vauquelin, of 18.8 of soda, 31.2 of acid, and 50 of water.

PHOSPHATE OF SODA is a salt important both in medicine and for some chemical purposes. It is prepared, by adding to the acidulous phosphate of lime, obtained from the decomposition of burnt bones by sulphuric acid, as much of a solution of carbonate of soda as may be sufficient to saturate the phosphoric acid, and dispose the liquor to crystallize. The lime, in combination with a portion of phosphoric acid, is precipitated, and the water holding dissolved the phosphate of soda is separated by filtration; by evaporation the salt is crystallized. The crystallization is difficult and indeterminate if there be any excess of acid, while with a slight excess of alkali it is easily effected, and the crystals are large and regular; hence it is in general slightly alkaline, so as to change to a green the syrup of violet. The form of the crystals is a rhomboidal prism, variously modified. They effloresce on exposure to the air, are soluble in three parts of cold water, and in half that quantity of boiling water. By heat, they are melted into a white opaque glass, which is soluble again in water. It consists, according to its analysis by Berzelius, of phosphoric acid 20.33, soda 17.67, water of crystallization 62: and abstracting the water, of 100 of phosphoric acid with 87 of soda. The taste of this salt is saline, without any bitterness. Hence it has been introduced into the practice of medicine as a substitute for the other aperient salts. As it melts easily, and promotes the fusion of earths and

metallic oxides, it is used as a flux, in analyses performed by the blow-pipe.

PHOSPHITE OF SODA is very soluble in water, requiring at a mean temperature only about twice its weight; its solution, by slow evaporation, affords on the edge of the vessel feather-like crystals, and in the liquor itself, crystals in the form of plates. Before the blow-pipe, it decrepitates, and gives a phosphorescent light; it is then melted into a glass, which appears opaque on cooling. It consists, according to Fourcroy and Vauquelin, of 23.68 of soda, 16.32 of acid, and 60 of water.

HYPO-PHOSPHITE OF SODA.—This salt, like the other hypo-phosphites, is stated by Dulong to be extremely soluble in water, and also abundantly soluble in alkohol.

BORATE OR SUB-BORATE OF SODA, the Borax of Commerce, is a salt which has long been in use in the arts. Homberg first obtained its acid, and Geoffroy discovered that it contained soda. It is a native production, being obtained from a lake in Thibet, from the sides of which it is dug up, and where there appears to be a constant reproduction of it. As a natural saline product, it is to be afterwards noticed. In the state in which it is imported, it is impure, from the presence of unctuous matter. It is purified by a process in some measure kept secret. Pelletier has shewn that the unctuous matter may be destroyed by calcination, and the salt obtained pure by solution and crystallization *. In the state in which it is met with in the shops, it is in the form of crystalline masses, of a figure irregular, but approaching to an hexaedral prism. This salt is not perfectly neutral; it contains an excess of soda, which seems necessary to cause it to crystallize; hence it changes the vegetable colours to a green. Its taste is cool and somewhat alkaline; it is soluble in 12

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* Mémoires de Chimie, tom. i, p. 82.

parts of cold, and in 6 parts of boiling water ; it is very slightly efflorescent. When exposed to a moderate heat, it melts from the water of crystallization it contains. When this is evaporated, there remains a spongy white mass, named Calcined Borax. If the heat be raised to ignition, this is melted into a pellucid glass, which suffers no decomposition, as it can be redissolved in water, and crystallized. It is decomposed by the greater number of the acids, and by potash and the earths, the former uniting with its alkali, the latter with its acid. According to Bergman it consists of 34 parts of boracic acid, 17 of soda, and 49 of water : according to Gmelin, of 35.6 of acid, 17.8 of soda, and 46.6 of water ; or abstracting the water, of 100 of acid and 50 of soda.

Borax fused with the more refractory earths combines with them ; and if there be a considerable excess of borax, the compound is soluble in acids ; hence its use in mineralogy, either in discovering the fusibility of minerals by the blow-pipe, or in facilitating mineral analysis. From this facility with which it melts and brings other substances into fusion, it is of use in some arts, as in making of glass, especially the finer glass for imitating the gems, and in soldering the more valuable metals, the borax melting, and covering the bright surfaces of the metals to be joined, so as to prevent their oxidation by the air.

The properties of the neutral borate of soda are little known. It may be prepared by adding the necessary quantity of boracic acid to a solution of borax ; the solution cannot be crystallized, but forms by evaporation a gelatinous mass : According to Gmelin, it contains three times as much acid as exists in borax.

Muriate of Soda.—This salt is one of the most abundant productions of nature, and exists native in greater quantity than any other neutral salt. The water of the ocean owes its saltness to it ; it is found in a number of mineral springs, and it forms immense strata in the earth.

Like the other muriates, it is, on the theory of chlorine be-
ing a simple body, regarded as a compound of it with sodi-
um.   When the sodium is placed in oxymuriatic gas, it
burns vividly, the gas is consumed, and the product is dry
muriate or chloride.   In the one doctrine this is consider-
ed as a simple combination, in the other the oxygen of the
oxymuriatic acid is held to combine with the sodium, con-
verting it into soda, with which the real acid combines.
When soda is saturated with muriatic acid, and the pro-
duct obtained by evaporation, and exposed to a red heat,
it is precisely the same ; and while in this case the soda is
considered in the old doctrine simply as combining with
the acid, the more complicated explanation is maintained
in the other, that the soda and the acid are mutually de-
composed, the oxygen of the one combining with the hy-
drogen of the other, and the combination being established
of the sodium with the chlorine.   The product, it has al-
ready been remarked, has all the properties of a neutral
salt.

Muriate of soda appears under the forms of Rock salt,
and Sea salt, according to its origin.   Rock salt is in ge-
neral pure muriate of soda, and when freed from its earthy
intermixture, and the small quantity of colouring matter,
by solution and evaporation, affords the salt in its purest
state.   The salt contained in saline springs is also in ge-
neral purer than that from the water of the ocean, though
not always so.   The proportion of muriate of soda contain-
ed in sea water varies in different latitudes.   The quan-
tity of saline matter on an average amounts to about $\frac{1}{25}$;
and of this rather more than $\frac{3}{4}$ths are muriate of soda.

The salt is procured by processes which are varied ac-
cording to situation.   In very cold climates, the water be-
ing received into shallow ditches during the winter is fro-
zen, and the liquor thus concentrated affords salt by eva-
poration.

In warm climates it is obtained by spontaneous evapora-

tion. The water is received into broad shallow trenches at the sea-side, without the reach of the tide. The bottom of these is made of clay well beaten, and they are divided into compartments; the fluid being spread out on an extensive surface, quickly evaporates; and by sluices it is removed from one space to another, so that when it arrives at the last, it is a strong brine, and the salt is soon deposited. Salt prepared in this manner is known by the name of Bay Salt.

In colder climates recourse must be had to artificial evaporation. The water is boiled down in shallow iron pans. Muriate of soda has the property of being as soluble nearly in hot as in cold water; it begins to crystallize therefore on the surface of the hot liquor; the crystals as they increase fall to the bottom of the vessel, are raked out, and set to drain. This is the process by which it is obtained in this country *.

Sometimes this method is conjoined with natural evaporation. The sea-water, before it is received into the boiler, is pumped into a reservoir, under which faggots of thorns, &c. are suspended. It is allowed to drop over these, and a large surface being thus presented to the atmosphere, while the air is rapidly renewed, much of the water is evaporated. It is then conveyed to the boiler, and evaporated. Or, the sea-water is made to flow over a bottom of clay covered with sand, which favours the evaporation of the water and the concretion of the salt; the saline deposite which is formed is lixiviated with sea-water, which becoming thus more impregnated with salt; is concentrated by boiling so as to afford it by hasty crystallization.

Sea-salt obtained by any of these processes is not pure.

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* Much valuable practical information with regard to the preparation and purification of salt, and its applications, is given in Dr Brownrigg's Treatise on the art of making Common Salt.

Sea water contains, besides muriate of soda, other neutral
salts, particularly muriates of magnesia and lime.   These
being more soluble in hot than in cold water, remain dis-
solved in the hot liquor, from which the salt crystallizes.
A small quantity of them, however, adheres to the mu-
riate of soda ; they render it deliquescent, give it a bitter
taste, and impair its antiseptic power.   Different pro-
cesses have been contrived to obtain it free from these fo-
reign salts.   The most simple is to procure it by slow eva-
poration, as it then crystallizes with less mixture of the
others.   This has been supposed to be the cause of the su-
perior purity of bay salt.   Hence also the larger the crys-
tals of sea-salt are, they may be supposed to be the purer,
as the largeness is owing to the slowness of the evapora-
tion by which they are formed.   Salt is thus obtained,
too, very pure, in large crystals, by evaporation by steam.

Another ingenious method was proposed by Lord Dun-
donald.   The salt to be purified is put into a conical ves-
sel, placed with the small end undermost, and having an
aperture at the bottom.   There is poured upon it a boiling
hot solution of common salt.   This dissolves any muriate
of lime, or of magnesia, or any other salt which may be
mixed with the sea-salt ; as the solution is saturated, none
of the latter is dissolved ; and by repeating the washing, it
is obtained nearly pure.   By three washings, it is render-
ed purer than salt prepared by any other process.   Ano-
ther method is to dissolve the salt, and again crystallize it.

Dr Henry examined the different kinds of this salt usu-
ally met with, principally with the view of ascertaining
how far the opinion is well founded that has generally pre-
vailed of the superiority of bay salt, prepared by sponta-
neous evaporation, to that prepared in this country.   Se-
veral specimens of the former were found to contain about
96 of muriate of soda in 100 parts, with small quantities
of sulphates of magnesia and lime, muriate of magnesia
and insoluble matter.   The sea-salt of this country, pre-

pared by hasty evaporation, contained about 93 of muriate of soda, with the same salts; that prepared by slow evaporation contained 97 parts in 100. Cheshire rock salt contained 98.3 of muriate of soda, and the same salt purified by solution and slow evaporation contained 98.6. These are purer therefore than bay-salt. Dr Henry found reason to conclude, that the superiority of antiseptic power in some of these salts compared with others, does not depend on superior purity of chemical composition, but rather on greater hardness, and on the larger size of the crystals, these circumstances retarding the solution of the salts from the presence of moisture. The purified Cheshire rock-salt appears to be fully equal to the foreign salt *.

For chemical purposes, muriate of soda is purified, by dissolving it in water, and adding to its solution a solution of carbonate of soda, till no cloudiness is produced by the addition. The strained solution may be crystallized.

Muriate of soda has a saline, rather agreeable taste ; it is soluble in less than 3 parts of water at 60°, according to Bergman in 2.8, according to Kirwan 2.5, and is scarcely more soluble in water at any high temperature, even to 212°, requiring at this temperature, according to Bergman, 2.76. Hence its hot solution does not crystallize by cooling ; the evaporation must either be carried on till the salt separates, or it must be left to spontaneous evaporation, when crystals form, which are cubes of a larger size and more regular as the evaporation has been more slow. These crystals neither deliquesce, nor effloresce ; the common sea-salt indeed is deliquescent, but this is owing to the muriates of magnesia and lime which adhere to it ; in a damp atmosphere, however, even pure muriate of soda is deliquescent. Exposed to heat the crystals decrepitate, from the sudden conversion of their water of crystallization into vapour. They lose, in general, according

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* Philosophical Transactions 1809.

to Henry, about 2 or 3 in 100 parts of weight; pure rock-
salt, however, does not lose any weight in a low-red heat,
nor does it decrepitate.   If the temperature is raised to a
red heat, the salt melts; in an intense heat it is volatiliz-
ed in white vapours, without undergoing decomposition.

Crystallized muriate of soda, dried at 80°, contains, ac-
cording to Kirwan, 53 of soda, and 47 of acid : accord-
ing to Berard, the salt after ignition is composed of 57 of
base, and 43 of acid.   Dr Marcet assigned as the propor-
tions 54 of base and 46 of acid; and Berzelius, those of
54.26 with 45.74.   Considering it as a chloride, and ta-
king Dr Marcet's proportions, it consists of 40.5 of so-
dium and 59.5 of chlorine.

This salt is decomposed by sulphuric and nitric acids,
which combine with its base.   None of the other acids de-
compose it in the humid way, but the phosphoric and bo-
racic effect its decomposition when assisted by heat, the
muriatic acid being more disposed than either of these
acids to assume the gaseous form, and this favouring its
evolution.   In all these cases, the presence of water is es-
sential to the disengagement of the acid.

One of the most important practical problems in che-
mistry is to decompose this salt, so as to obtain its alkali.
It abounds so much in nature, that if such a process could
be carried on to advantage, a vast supply of soda would be
obtained; and as this alkali can be employed for every
purpose that potash can, and is superior to it for some
uses, such a discovery would be of much importance to the
chemical arts.   Different methods have been employed.

Lime produces a partial decomposition, either when
pure or combined with carbonic acid, but it is slow and
soon ceases from the muriate of lime produced counteract-
ing the formation of carbonate of soda, or decomposing
it if it were formed.   By the soda receiving carbonic acid
from the atmosphere, and efflorescing above the mass, a
certain quantity can indeed be procured; and in this way,

Berthollet has shewn that the formation of carbonate of soda, in some natural situations, takes place. But the quantity of materials that would be requisite, and the length of time necessary to the decomposition being complete, prevent it from being applicable in practice.

Potash in the state of the potash of commerce has been used as the medium of decomposition. There is here indeed the obvious objection, that we only substitute one alkali for another. Still, from local circumstances, this process can often be followed with advantage. Though the decomposition must be partial, it appears from the experiments of Westrumb, that the product of soda is considerable: 20 lbs. of sea-salt are dissolved in 60 lbs. of water, and 25 lbs. of the potash of commerce added, boiling the liquor until a saline pellicle forms on its surface: on allowing it to cool, much muriate of potash is deposited. When cooled to 50°, on removing it into another vessel carbonate of soda crystallizes; and from the above quantity of ingredients, 25 lbs. at an average are obtained, which however requires, by solution and crystallization, to be freed from a little muriate of soda adhering to it, by which it is reduced to 20 lbs [*]. As muriate of potash is as useful as the carbonate in the manufacture of alum, or the preparation of nitre, where it can be applied to these uses, this process may be advantageously followed, as it may also where potash is recovered in an impure state from certain processes in the arts in which it is employed, as from the ley remaining in the manufacture of soap.

Another decomposition of muriate of soda is that by the medium of oxide of lead. Scheele observed, that in mixing four parts of oxide of lead with one part of sea-salt, making the mixture into a paste with water, and allowing it to stand in a soft state for a little time, adding water occasionally to keep it in this state, the oxide of lead attract-

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[*] Annales de Chimie, tom. vi. p. 21 ; tom. xiii, p. 213.

ed the muriatic acid, and the soda might be extracted
by washing the mass with water This method has been
carried into practice, sea-salt and litharge being triturated
together, and afterwards lixiviated, and the soda being com-
bined with carbonic acid so as to be obtained under the
form of the crystallized carbonate, either by leaving the
solution exposed to the atmosphere, or by evaporating and
calcining the saline matter with charcoal or saw-dust, at a
red heat, from which carbonic acid is formed, and attract-
ed. The drawback on the process is the large quantity of
oxide of lead which is required: three or four parts are
necessary to decompose fully one of muriate of soda. The
submuriate of lead may, by the application of heat, be con-
verted into a yellow pigment *, but the demand for this is
not sufficiently extensive to admit of the process being car-
ried on on a large scale. The submuriate of lead may, by
roasting, and calcination with charcoal, be reduced to the
metallic state ; but the expence of oxidating the lead, and
then reducing it, is such as to render the method generally
impracticable. In some cases only where lead contains sil-
ver, and is oxidated to obtain that metal, advantage is ta-
ken of this, and the two operations are combined.

The most practicable method, on the whole, is decom-
posing the muriate of soda by sulphuric acid, and after-
wards decomposing the sulphate of soda by carbonaceous
matter with various additions, such as lime, iron, &c. This
gives rise to several varieties of the general process, an ex-
cellent summary of which, as well as of the other methods,
was given in a report on this subject by Lelievre, Pel-
letier, D'Arcet, and Giroud †. The outline of the process
is to decompose the muriate of soda in the usual mode by
sulphuric acid, the muriatic acid being collected for any
useful purpose to which it can be applied. The sulphate

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* Repertory of Arts, vol. xii, p. 157.
† Annales de Chimie, tom. xix.

of soda is calcined in a reverberatory furnace, to free it from superfluous acid : it is then decomposed by exposing it to heat with charcoal, or any other carbonaceous matter, the charcoal attracting the oxygen of the acid. It is necessary, however, to add some substance to attract the sulphur, which would otherwise combine with the alkali, and be only imperfectly expelled by heat. Lime may be used, the sulphate of soda being mixed with an equal weight of chalk, and rather more than half its weight of charcoal in powder, and exposed to heat in a reverberatory furnace, sufficient to produce a state of imperfect liquefaction, the matter being frequently stirred to facilitate its explosion : after the mass has been exposed to a humid atmosphere, carbonate of soda is extracted from it, 100 lbs. affording $37\frac{1}{2}$ lbs. of the carbonate crystallized. This, in the opinion of the authors of the preceding report, is the process which, where peculiar local circumstances do not favour any of the others, is the best. Iron is also used. A process of this kind described in this report, consists in mixing sulphate of soda calcined 200 lbs., charcoal, partly in powder and partly entire, 62 lbs., and pieces of white iron or iron plate, 65 lbs. ; the mixture of salt and charcoal being exposed to heat, and the iron added in successive portions, is at length brought completely into fusion ; after being cold it is lixiviated, and affords from 100 lbs. of salt, 71 lbs. of crystallized carbonate of soda, the residual matter being sulphuret of iron with a little charcoal. Instead of iron, some varieties of iron ore of the hæmatitic kind may be used, or the muriate of soda may be decomposed by sulphate of iron instead of pure sulphuric acid. Both iron and lime too may be used with advantage at the same time : And these processes have been combined in various modes, for which, in this country, patents have often been obtained *.

In any of these processes, the soda obtained is not pure,

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* Philosophical Magazine, vol. xxiii, p. 70.

but contains a little sulphur, which, by passing to the state of sulphurous acid by absorbing oxygen, diminishes the alkaline power. Dizé stated, that oxide of lead is capable, in the humid way, of abstracting the greater part or the whole of the sulphur, a quantity of it in powder being added to the solution of the saline matter boiling. Oxide of manganese was substituted with equal success: it is cheaper, and it has the advantage that it can be repeatedly used, by calcining it each time, so as to expel the sulphur *.

Muriate of soda is of extensive use. Its application to preserve animal substances from putrefaction is well known; the theory of its antiseptic quality has never been properly explained. It is also taken universally as a seasoning to food, and seems to be necessary to promote digestion, as even the lower animals languish when deprived of it. It is employed in a variety of arts. In the manufacture of pottery, it serves as a glazing, when it is thrown into the oven in which the ware is baked, probably by the alkali combining with the earthy matter. It is employed in the manufacture of glass, which it is said to render whiter and clearer; in that of soap, which it makes harder; as a flux in the melting of metals from their ores; and in a variety of chemical and pharmaceutical processes.

OXYMURIATE OF SODA.—The relation of soda to oxymuriatic acid, there can be no reason to doubt is similar to that of potash, but the properties of oxymuriate of soda have not been examined.

HYPER-OXYMURIATE OR CHLORATE OF SODA.—This salt is prepared in the same manner as the preceding, but it is difficult to obtain it free from the muriate of soda which is formed with it, as they are nearly of the same degree of solubility in water. Chenevix obtained it by treating with alkohol the entire salt: the hyper-oxymuriate, by repeated solution in that fluid, and crystallization from it, was ob-

* Repertory of Arts, vol. iv, vi, vii, ix, x.

tained pure. It is soluble in three parts of cold, and less of warm water; is slightly deliquescent, crystallizes in cubes, or rhomboids. Its taste is cool. It is decomposed by heat; and its relations to the acids, and to combustible bodies, are similar to other hyper-oxymuriates. According to the analysis of it by Chenevix, it consists of hyper-oxymuriatic acid, 66.2 parts; soda, 29.6; and water, 4.2. Vauquelin prepared this salt by adding directly chloric acid to carbonate of soda; it is so soluble, that its solution he found did not crystallize until evaporated nearly to the consistence of syrup; it then afforded plates similar to those of chlorate of potash; he found it not deliquescent; it melts rapidly on burning fuel, producing a yellow light; and by distillation affords a large quantity of oxygen.

FLUATE OF SODA is less sapid than fluate of potash; it decrepitates when heated, and suffers the igneous fusion; it is neither deliquescent nor efflorescent, is rather more soluble in hot than in cold water, and its solution on cooling affords minute crystals. Sulphuric acid decomposes it with effervescence, and it suffers the same decomposition as fluate of potash from the earths *.

SILICEO-FLUATE OF SODA.—Scheele had described the action of siliceo-fluoric acid on soda as similar to that on potash; but according to Gay-Lussac and Thenard it is very different. When a solution of soda is poured into the liquid acid, no precipitate is formed, but when the liquor is heated, it forms a transparent jelly: the gelatinous matter, separated by a filter, is pure silica; and the filtered liquid is pure fluate of soda.

HYDRIODATE OF SODA is described by Gay-Lussac as being obtained in large flat rhomboidal prisms, which contain a considerable quantity of water of crystallization, and yet are deliquescent. This water is expelled by heat, the salt is melted and is partially decomposed, so as to become

* Gay-Lussac Recherches Physico-Chimiques, tom. i.

alkaline; 100 of water at the temperature of 60° dissolve
173 of the salt: when dried it is considered by Gay-Lus-
sac as an ioduret, the hydrogen of the acid combining with
the oxygen of the soda and forming water, while the so-
dium combines with the iodine. This ioduret is composed
of 100 of iodine with 18.5 of sodium; the undecomposed
hydriodate consists of 100 of acid with 27.7 of soda.

OXIODATE OF SODA crystallizes in minute aggregated
prisms, or grains of a cubic form; which contain no water
of crystallization, and are not altered by exposure to the air;
100 of water at 60 dissolve 7.3 parts; they deflagrate on
burning fuel at a heat somewhat below redness. From
decomposition by heat about 24.45 of oxygen are given out
from 100 parts; and hence Gay Lussac infers, that the salt
consists of this proportion of oxygen with 75.76 of ioduret
of sodium. When iodine is put into a solution of soda a
salt is obtained in six-sided prisms, very alkaline, which he
considers as sub-oxiodate of soda: and a similar salt is
formed by adding soda to the neutral oxiodate.

In its physical and more obvious chemical properties,
soda is very similar to potash. They are easily distin-
guished, however, in their combinations. The salts which
soda forms with acids are entirely different from those of
which potash is the base. Though soda saturates a lar-
ger portion of acids in general than potash, its salts are
decomposed, at least partially, by potash. There is one
test convenient to distinguish them, the solution of muriate
of platina, this giving a precipitate with potash or any of
its salts, which it does not do with soda.

Soda is applied to the same purposes in the arts as pot-
ash, and in general is preferred to the potash.

Soda is a principle in several earthy fossils. Dr Kenne-
dy discovered it in lava, and in trap and greenstone. Kla-
proth found it in cryolite, in the proportion of 36 in 100;
and it has since been found in a number of other minerals,
besides, in its native saline compounds.

CHAP. IV.

OF LITHINA.

THIS, I have already remarked, has been announced as a newly discovered body belonging to the class of alkalis. It was found by Arfvredson, a Swedish chemist associated with Berzelius, in a mineral named Petalite, first observed in the mine of Uto in Sweden, by D'Andrada. It exists in this mineral in the quantity of about 5 *per cent.* combined with about 17 of alumina and 78 of silica, and was discovered in the analysis from its great capacity of saturation. It has since been detected in another mineral, Spodumene or Triphane, to the amount of 8 *per cent.* The discovery of this new alkali has been confirmed by Vauquelin, who has repeated and established the experiments of Arfvredson, and has added some facts with regard to it. And Sir H. Davy has succeeded in reducing it to the metallic state. From being found in the mineral kingdom, Berzelius gave it the name of Lithina. It has a much greater resemblance to soda than to potash, and its metallic base, to which the name of Lithium will belong, is nearly allied to Sodium.

Lithina is extracted from petalite by the usual process by which alkalis are detected in mineral analysis,—subjecting the mineral to calcination with nitrate or carbonate of barytes, precipitating the barytes, and the other earths, and obtaining the alkali in combination with an acid. No full account has been given of its properties, but the following are stated as its characteristic qualities.

Its capacity of saturation in relation to acids is superior

to that of the other alkalis, and even to magnesia,—the circumstance which first led to its discovery, the salt formed by its combination with an acid in the analysis of the petalite much exceeding in weight that which would have been formed from potash or soda. Its equivalent number, or combining quantity, is stated by Vauquelin at 22.97, that of its metallic base at 12.97, of its dry sulphate 72.97, and its crystallized sulphate 82.97. It contains in 100 parts, according to Vauquelin, 43.5 of oxygen, according to Berzelius 43.9,—a proportion much greater than that in potash or soda.

The greater number of its salts are very soluble in water, and also very fusible. The Carbonate melts at attaining a red heat; and if it is in a platina crucible, the alkali acts with as much energy on the platina, as nitrate of potash or soda does; it does not dissolve readily in water, but it gives a taste similar to that of the other alkalis, and when the solution is evaporated, the salt crystallizes in very small prisms. The Nitrate crystallizes in rhomboids, and attracts moisture rapidly. The Muriate is also very deliquescent, even more so than muriate of lime. The Sulphate crystallizes readily, and the crystals contain no water of crystallization. Both the sulphate and muriate liquefy long before they are heated to redness. These salts are not precipitated either by tartaric acid or by muriate of platina.

It combines with sulphur, and forms a yellow coloured sulphuret abundantly soluble in water [*].

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[*] Annales de Chimie et Physique, t. vii, p. 199, &c.
Annals of Philosophy, vol. xi, 291, 373, 448.

APPENDIX TO VOLUME SECOND.

The following Memoirs contain the illustrations and proofs of the doctrine I have explained with regard to the theory of the constitution of acids and of alkalis, and which, as conveying a connected view of the subject, with details more ample than could with propriety be introduced in the body of the work, I proposed (page 167.) to add as an Appendix to the present volume. The first of these Memoirs is from the Ninth Volume of the Transactions of the Royal Society of Edinburgh. The second, read at a subsequent period as a continuation of the other, has not been before published. I have omitted a preliminary account of some experiments, on the production of water from muriatic acid, as being sufficiently referred to, page 429. of this volume. What follows, therefore, commences with the second part of the first Memoir, illustrating the theory.

OBSERVATIONS ON THE CHEMICAL CONSTITUTION OF MURIATIC ACID GAS, AND ON SOME OTHER SUBJECTS OF CHEMICAL THEORY.

ADMITTING water to be procured from muriatic acid gas in those forms of experiment, direct or indirect, in which the agency of no other substance that can afford it, is introduced, the conclusion seems necessarily to follow, which forms the basis of one of the two systems under which the relations of oxymuriatic and muriatic acids have of late years been explain·d, —that oxymuriatic acid is a compound of muriatic acid with oxygen ; and that muriatic acid in its gaseous state contains combined water. This doctrine, accordingly, may be maintained, and may even perhaps be just. It is not, therefore, from the consideration of any deficiency in its support, that I depart from it in the following observations, but that I consider the view I have to propose as perhaps more probable, or at least as, on the whole, according better with the present state of chemical theory. In a science such as Chemistry, the principles of which rest, rather on probable evidence, than on demonstration, it is of importance to present a subject in every point of view under which it may be surveyed ; and this must serve as an apology for the speculations I have now to offer.

There are, I believe, only two arguments to which any weight is due in support of the opinion that chlorine is a simple substance, which by combination with hydrogen forms muriatic acid. One is drawn from the analogy resting on the general fact, sufficiently established, that acidity is in different cases the result of the agency of hydrogen ; the other, from the analogy in the chemical relations of chlorine and iodine.

Sulphur forms with hydrogen a compound unequivocally acid. The compound radical of prussic acid, Cyanogen, discovered by the able researches of Gay-Lussac, likewise acquires acidity when it receives hydrogen. Acidity, therefore, is a property not exclusively connected with oxygen; it is also communicated by hydrogen; and when chlorine with hydrogen gas forms muriatic acid gas, the agency exerted may be considered as similar to that arising in other cases, of the production of an acid from the action of hydrogen.

This is confirmed by the relations of iodine. It, too, forms an acid by combination with hydrogen; and the chemical agencies of iodine are in several other respects similar to those of chlorine. When the one, therefore, is considered as a simple body, (and there is no absolute proof that iodine is a compound,) the other is, with probability, placed in the same class. And certain analogies existing between sulphur and iodine serve to connect and confirm these views. Each of them forms an acid with hydrogen; each of them also forms an acid with oxygen. But chlorine exhibits precisely the same points of resemblance : with hydrogen, it forms muriatic acid; with oxygen, it forms chloric acid. Its chemical relations, with regard to acidity, being thus similar, seem to require the same explanation to account for them.

These facts lead undoubtedly to views of chemical theory different from those which had before been established, and on which the old doctrine with regard to the nature of muriatic and oxymuriatic acids rests. It may be well, therefore, to inquire how far they may modify the conclusions to be drawn, admitting even that oxymuriatic acid contains oxygen, and that muriatic acid gas affords water.

When water is obtained from muriatic acid gas, it does not necessarily follow that it has pre-existed in the state of water. It is equally possible, *a priori*, that its elements may be present in simultaneous combination with the acid, or its radical, —that the acid is a ternary compound of a radical with oxygen and hydrogen; and that it is decomposed in those proces-

ses by which water is procured, the hydrogen, with the requisite proportion of oxygen, combining to form water; and its radical, with any excess of oxygen, remaining in union with the substance by which the change has been effected.

If this view were adopted with regard to muriatic acid, the same view might, on the same grounds, be applied to the other acids which appear to contain water in intimate combination, and in a definite proportion. And such an acid, the radical and precise constitution of which are known, may be best adapted to illustrate the hypothesis.

Sulphuric acid affords water when it is submitted to the action of an alkaline base; and the quantity of this water appears to be definite, amounting to 18.5 in 100 of the strongest acid which can be procured in an insulated state; 100 parts of this acid, therefore, are considered as composed of 81.5 of real acid, (consisting of 32.6 of sulphur, and 48.9 of oxygen,) with 18.5 of water. But if, instead of this view of its constitution, it be considered as a ternary compound of sulphur, oxygen, and hydrogen, its composition will be 32.6 of sulphur, 65.2 of oxygen, and 2.2 of hydrogen. In those processes by which water is obtained from it,—in the action, for example, of an alkaline base, and subsequent exposure to heat, the composition is subverted by the affinities exerted; the hydrogen unites with the requisite proportion of oxygen, forming water, and the remaining oxygen with the sulphur unite with the base. In the action of a metal on the acid, there is the same result; only by the attraction of the metal to oxygen, the whole of that element is retained, and the hydrogen is disengaged.

Muriatic acid gas, then, according to this doctrine, is the real acid, a ternary compound of a radical (at present unknown) with oxygen and hydrogen, exactly as sulphuric acid, in its highest state of concentration, is the real acid, a ternary compound of sulphur, oxygen, and hydrogen. When it is submitted to an alkaline base, the action exerted causes its decomposition; its hydrogen, and part of its oxygen, combine to form water, and its radical, with its remaining oxygen, unite

with the base, forming a neutral compound, analogous to what other acids of similar constitution form. When a similar result is obtained from the action of a metal, its whole oxygen must be considered as retained, and its hydrogen is liberated.

Nitric acid in its highest state of concentration is not a definite compound of real acid with about a fourth of its weight of water; but a ternary compound of nitrogen, oxygen, and hydrogen. Phosphoric acid is a triple compound of phosphorus, oxygen, and hydrogen; and phosphorous acid is the proper binary compound of phosphorus and oxygen. The oxalic, tartaric, and other vegetable acids, are admitted to be ternary compounds of carbon, oxygen, and hydrogen, and are therefore in strict conformity to the doctrine now illustrated.

A relation of the elements of bodies to acidity is thus discovered, different from what has hitherto been proposed. When a series of compounds exists, which have certain common characteristic properties, and when these compounds all contain a common element, we conclude with justice that these properties are derived more peculiarly from the action of this element. On this ground Lavoisier inferred, by an ample induction, that oxygen is a principle of acidity. Berthollet brought into view the conclusion, that it is not exclusively so, from the examples of prussic acid and sulphuretted hydrogen. In the latter, acidity appeared to be produced by the action of hydrogen. The discovery by Gay-Lussac, of the compound radical cyanogen, and its conversion into prussic acid by the addition of hydrogen, confirmed this conclusion; and the discovery of the relations of iodine still farther established it. And now, if the preceding views are just, the system must be still farther modified. While each of these conclusions is just to a certain extent, each of them requires to be limited in some of the cases to which they are applied; and while acidity is sometimes exclusively connected with oxygen, sometimes with hydrogen, the principle must also be admitted, that it is more frequently the result of their combined operation.

There appears even sufficient reason to infer, that from the united action of these elements, a higher degree of acidity is

acquired than from the action of either alone. Sulphur affords a striking example of this. With hydrogen it forms a weak acid. With oxygen it also forms an acid, which, though of superior energy, still does not display much power. With hydrogen and oxygen it seems to receive the acidifying influence of both, and its acidity is proportionally exalted.

Nitrogen with hydrogen forms a compound altogether destitute of acidity, and possessed even of qualities the reverse. With oxygen in two definite proportions, it forms oxides; and it is doubtful, if in any proportion it can establish an insulated acid. But with oxygen and hydrogen it forms nitric acid, a compound more permanent, and of energetic action.

Carbon with hydrogen forms compounds which retain inflammability without any acid quality; with oxygen it forms first an inflammable oxide, and with a larger proportion a weak acid. But, combined with both hydrogen and oxygen, in different proportions, it forms in the vegetable acids compounds having a high acidity. These acids, therefore, are not to be regarded, according to the theory of Lavoisier, as composed of a compound base of carbon and hydrogen, acidified by oxygen, but of a simple base, carbon, acidified by the joint action of oxygen and hydrogen.

Muriatic acid itself presents the same result. Oxymuriatic acid must be considered, according to this doctrine, as a compound of an unknown radical, (*Murion*, if the term may be allowed,) with oxygen, analogous in this respect to sulphurous acid, except that in the latter there is an excess of base, in the former an excess of oxygen : And oxymuriatic acid, with the addition of hydrogen, forms the ternary compound muriatic acid, as sulphurous acid with the same addition forms hydrosulphuric acid, with a deposition of the excess of sulphur. There is, accordingly, the strictest analogy between muriatic acid and those other acids, the sulphuric, nitric, &c. which contain both oxygen and hydrogen; while there is none, as Berzelius remarked, between it and those, such as the prussic acid or sulphuretted hydrogen, which contain merely hydrogen. This principle solves the difficulty which has always presented

itself in the relation of muriatic and oxymuriatic acids on La-
voisier's theory of acidity,—that the latter, though it has re-
ceived an addition of oxygen, is inferior in acid power to the
former. It is so precisely as the binary sulphurous acid is one
of less energy of action than the ternary hydro-sulphuric acid,
or as the carbonic is less powerful than the oxalic acid The
proper analogy is that of the oxymuriatic with the sulphurous
acid, and the muriatic with the sulphuric ; and under this point
of view there is no anomaly, but strict conformity. And thus
also is accounted for, what is at variance with the hypothesis
of Gay-Lussac, the total want of analogy between chlorine and
sulphur, which he classes together, except in the single cir-
cumstance of acidity being communicated to both by hydro-
gen ; while there exists a close analogy between sulphurous
acid and oxymuriatic acid, in their most essential properties,—
their gaseous form, their specific gravity, their suffocating o-
dour, their power of destroying vegetable colours, their solu-
bility in water, their remaining combined with it in congela-
tion ; their acidity, their combining weights, and their being
attracted to the positive pole of the voltaic series ; and any de-
viation from this analogy evidently arises from the excess of
oxygen in oxymuriatic acid *.

It is obvious, that it would be in vain to seek for the disco-
very of real muriatic acid in its insulated form. It exists no
more than real sulphuric or real nitric acid. The oxygen and
sulphur, or oxygen and nitrogen in union with a salifiable base
in the sulphates and nitrates, may not be in direct combina-

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* It is curious with regard to the most important of these analogies, that
of the equivalent or combining weights, that oxymuriatic acid stands next to
sulphurous acid ; the former in Dr Wollaston's scale being 44, while the lat-
ter will be found to be 40. The acidity of oxymuriatic acid is fully establish-
ed by the most unequivocal acid property, that of combining with alkalis, and
forming neutral compounds. The saline nature of these compounds had
been shewn by Berthollet ; that with lime has been demonstrated by Mr Dal-
ton, who also pointed out the probability, from the results by double decom-
position, that the acid combines in a similar manner with other salifiable bases ;
and the existence of these compounds has been established by Mr Wilson.

tion, nor capable of existing as a separate binary compound. The insulated binary compound of the radical of muriatic acid with oxygen is oxymuriatic acid, as the binary compound of sulphur and oxygen is sulphurous acid, and of nitrogen and oxygen, nitrous and nitric oxides.

Iodine, the discovery of which and its relations has for a time given predominance to the new doctrine of chlorine, conforms sufficiently to these views. Some have considered it as a body belonging to the same class as chlorine ; others regard it as more analogous to sulphur. It has little analogy to either, except in the property of forming acids with oxygen and with hydrogen. It differs remarkably from chlorine in its comparative inertness, its solidity, specific gravity, and great weight of its equivalent quantity. And it differs from sulphur in its want of inflammability, its solubility in water, and its being attracted to the positive pole of the voltaic series. All these analogies are preserved, and its relations connected, by considering it as an oxide, which, both from its specific gravity, the colour of its compounds, and the great weight of its equivalent quantity, has probably a metallic base ; and which acquires acidity by an addition of hydrogen on the one hand, and on the other by the addition of oxygen, or of oxygen and hydrogen. In these respects, and in many of its chemical properties and relations, a considerable analogy exists between it and oxide of arsenic, or oxide of tellurium. Or if it were to be classed as a simple substance, (on the ground of its not having been decomposed,) which forms an acid with hydrogen, and another with oxygen and hydrogen, it does not in these respects offer any deviation compared with other acidifiable bases, or afford an argument of much weight in support of the undecomposed nature of chlorine.

The doctrine I have illustrated affords a satisfactory explanation of the properties of the compounds formed by oxymuriatic acid with certain inflammables, particularly with sulphur and phosphorus. These undoubtedly present an anomaly in the other views that have been given of their constitution. In the old doctrine they are considered as compounds of two real

acids ;—one of muriatic, with phosphorous or phosphoric acid, the other of muriatic, with sulphurous or sulphuric acid. But they have none of the properties which would be looked for in such a combination; they have no acidity, or if any appear in one of the compounds with phosphorus, it is to a very limited and doubtful extent; and they are substances even which have little energy of chemical action. In the new doctrine they are considered as compounds of chlorine with their bases, sulphur and phosphorus. Of course, as these bases form powerful acids with oxygen, and as chlorine is considered as an element of similar agency as oxygen, communicating similar powers, and conferring acidity even on hydrogen, they might, with not less reason than on the other doctrine, be expected to be acids of the greatest strength. The view I have stated accounts for their characters. They are ternary compounds, of the radical of muriatic acid with the particular inflammable,—sulphur, or phosphorus, with oxygen. The oxygen is not in sufficient quantity to communicate acidity, or, in one of the combinations of phosphorus, does so only to a very slight extent. But when water is added, a sufficient proportion of oxygen is supplied to produce this result, and the acidity is exalted by the corresponding hydrogen entering into the combination. What has been called Phosgene Gas, procured under certain circumstances from the action of oxymuriatic gas and carbonic oxide, may be regarded as of a similar nature, the agency of a small portion of water or of hydrogen being probably essential to its formation, a circumstance which serves to account for the discordant results with regard to its production *.

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* The difficulty of entirely excluding water and hydrogen from the constituents of this gas is sufficiently apparent. And the fact, that it cannot be formed from them by the action of the electric spark, but only by the continued action of solar light, is favourable to the above opinion. The conversion of carbonic oxide into carbonic acid, by the joint action of oxymuriatic gas and hydrogen, an experiment which I performed when the new hypothesis with regard to the nature of chlorine was brought forward, and which was attempted to be invalidated by some singular controversial methods, I consider as depending probably on the same principle.

It deserves remark, that while there runs through the whole
series of acidifiable bases in relation to their combinations with
oxygen and hydrogen, a general analogy, there is also some
deviation, and something with regard to each that is specific.
Sulphur affords the most perfect example of their agency.   It
forms an acid with hydrogen ; it forms another with oxygen ;
and a third, still more powerful, from the joint action of oxy-
gen and hydrogen.   Carbon forms an acid with oxygen ; it also
forms a series of acids of greater strength with oxygen and hy-
drogen ; it acquires no acidity, however, from hydrogen alone ;
and with an inferior proportion of oxygen it forms an oxide.
Phosphorus bears a strict analogy to sulphur, except that its
combination with hydrogen does not give rise to acidity, a cir-
cumstance in which it resembles carbon.   Nitrogen is peculiar
in forming two oxides with different definite proportions of
oxygen ; it is doubtful if it forms a free acid with oxygen a-
lone ; but it conforms to the general law, and forms a powerful
acid with oxygen and hydrogen.   Assuming the existence of a
simple radical of muriatic acid, it resembles sulphur, phospho-
rus and carbon, in forming an acid with oxygen, and one still
more powerful with oxygen and hydrogen ; but it differs in the
peculiarity, that the proportion of oxygen to the base in the
binary combination is the same as it is in the ternary, so that
the addition of hydrogen converts the one into the other ;
and also in its combining apparently with more numerous
proportions of oxygen than any of the other acidifiable bases,
—two circumstances which, as well as the difficulty of ef-
fecting its decomposition, probably depend on the same cause,
the strength of its attraction to oxygen.   The fluoric are si-
milar to the muriatic compounds, except that the binary com-
pound of the radical with oxygen cannot be obtained in an in-
sulated form, and that its combinations with oxygen are less
numerous.   The relations of iodine or its radical are similar to
those of the radical of muriatic acid, or perhaps rather to sul-
phur, except that its binary compound with oxygen does not
appear to have acidity, in which it approaches to the metals.
The metals usually combine with oxygen so as to form oxides ;

some of them also form acids with oxygen, or with oxygen and hydrogen; and these last usually also combine with hydrogen alone. This fact, of some of the metals forming acids, is so far an anomaly, since their compounds with oxygen rather form alkalis, and no other substances give rise to both results; the greater number of the substances, too, which form acids with oxygen or hydrogen, are evidently, from the smallness of their combining quantities, not of a metallic nature. Still the connection between the two classes is in some measure established on the one hand, by nitrogen, which with hydrogen forms an alkali, and on the other by iodine, which has properties and relations common to both.

In some cases it is probable, that there is a variation in the proportions of these ternary combinations, giving rise to a diversity of products, which exist only in combination with those bodies by which their formation is determined, and, being modified by any process causing their evolution, are not easily observed. It is doubtful if the same base in any case forms different acids by combination with oxygen in different proportions, or by combination with hydrogen in different proportions. But the example of the vegetable acids seems to shew that this may occur in the united action of oxygen and hydrogen; carbon acidified by different proportions of these elements constituting the composition of these acids. Other bases may present similar results. The radical of muriatic acid may unite with other proportions of oxygen and hydrogen than those which form muriatic acid; and this might afford a solution of the theoretical difficulty of the production of water in the experiments in the first part of this memoir, independent of the explanation of it from the formation of a super-muriate. A compound may be formed with less oxygen and hydrogen than what exist in muriatic acid, in combination with the metal acted on, and thus a portion of water may be liberated. Nor will it be easy to establish this by any difference in the product, as it can scarcely be submitted to any examination, but by processes which change the result. The chloric acid which, according to Gay-Lussac, cannot exist insulated with-

out water, may be in like manner a ternary compound of these elements in other proportions. Prosecuting the same analogy, the glacial or fuming oil of vitriol may be, not what has lately been asserted, real sulphuric acid, (for probably no such substance as that to which this term has been applied, can be obtained insulated,) but a compound of sulphur with oxygen and hydrogen, in proportions different from those which constitute common oil of vitriol. Nitrous acid, if it cannot be formed without water, may be a compound of nitrogen with a smaller proportion of oxygen and hydrogen, than nitric acid. And some of the acids lately described, of which phosphorus is the base, may arise from variations of proportions of this kind.

The view which I have now illustrated, I must add, is not to be regarded as mere speculation. The evidence in support of it is just as conclusive as that from which the opposite opinion is inferred. The obtaining water from a compound is no necessary proof that water pre-existed in it; and conversely, the causing water to enter into combination in a compound is no necessary proof that it remains in the state of water in the product. In many cases we draw the reverse conclusions, considering water as being formed where it is obtained, and as decomposed where it is communicated. And in the case of its relation to acids, it will be found that there is no strict evidence of its existing as water in combination with what is considered as the real acid : and of course the conclusion is equally open to be drawn, that it exists in these combinations in the state of its elements, and that when obtained, it is a product of a change of composition.

It is even more probable, *a priori*, that the ultimate elements should act on each other where energetic affinities are evidently exerted, than the immediate principles, and the relations of these elements will determine the combinations, and the proportions. And by admitting this view, we avoid the anomaly which is presented in ascribing to the agency of water effects so different from those to which it usually gives rise. In general, water operates on bodies simply as a solvent, overcoming cohesion in solids, diluting liquids, or absorbing gases, with-

out otherwise modifying their properties, or communicating to them any important chemical powers. But in the particular cases now referred to, it is supposed to produce the effects of the most energetic chemical agent ; it enters into combination in proportions strictly definite, is retained by the most powerful affinities ; communicates new and characteristic properties ; and is essential even to the existence of these compounds, in an insulated form. Berzelius and Gay-Lussac have stated, that it is to be considered as a base necessary to retain the elements of the acid combined, though without neutralising the acid properties,—an opinion which in itself, and still more with this condition, is certainly sufficiently incongruous. And both theories admit equally of incongruity in the supposed presence and energetic action of water in acids. The old doctrine admits its influence in sulphuric, nitric, phosphoric, and muriatic acids, though at variance with its principle, that oxygen is the element which confers acidity, or at least having no conformity to that principle, nor receiving explanation from it. The new doctrine refuses to admit it with regard to muriatic acid, but admits it in all the others,—an exception which serves only to render the system more objectionable by the violation of analogy ; while the admission with regard to the others is equally incapable of being accounted for on any principle it affords. By considering oxygen and hydrogen as elements conferring acidity, a satisfactory solution is afforded of the effects produced in these cases by their joint operation ; and independent of this, it is much more probable, *a priori*, that such effects should arise from the action of elements so powerful, than from the agency of water, which, in its general relations, exerts such feeble powers. Lastly, The principle on which the presence of combined water in these acids has been supposed to depend,—that of the strong attraction of the acid to water, seems altogether fallacious ; for on this principle sulphurous acid should also contain combined water, and sulphuretted hydrogen, and even carbonic acid, might be expected to retain a small portion. The whole evidently depends on difference of constitution. Sulphurous acid, sulphuretted hydro-

gen, and carbonic acid, are binary compounds, and therefore yield no water, nor retain any in intimate combination ; and in the others, the proportion of water supposed to exist will be found to have no relation to the attraction of the acid to water, so far as this can be inferred, as is evident from phosphoric acid affording as much as sulphuric or nitric. This affords nearly a demonstration, that the constitution is that of simultaneous combination of the elements, and not of water and acid.

That water may also exist in immediate combination with acids, without being resolved into its elements, is sufficiently possible ; and it probably is in this state, in those cases in which there are no indications of an intimate combination, or definite proportion. It may then be considered as in solution similar to that in which it holds salts dissolved, or, what is a closer analogy, similar to that in which it holds dissolved the vegetable acids, which are admitted to be ternary compounds of carbon, hydrogen, and oxygen. The opposite view applies only to that portion of water considered as essential to the body in an insulated state, and in which it is combined in a definite proportion, observing in its relations, or the relations of its elements, equivalent proportions to other bodies.

In the last place, Considering this opinion in relation to the two opposite views which have been maintained with regard to the constitution of oxymuriatic and muriatic acids, while it has all the evidence in its favour from which the existence of water in muriatic acid gas is inferred, and all the analogies by which this is confirmed ; it has the support which the doctrine of the undecompounded nature of chlorine derives from the relations of sulphur, iodine, and cyanogen : and from the induction that hydrogen, as well as oxygen, communicates acidity. It avoids, at the same time, the improbability which attends that doctrine, in its leading principle, that muriatic acid contains no combined water, though other powerful acids are held to contain it, and though it affords water by the very same processes by which they yield it ; and in the still greater violation of analogy, (the most extraordinary perhaps ever admitted in chemical reasoning,) involved in the conclusion, that the com-

pounds which this acid forms with salifiable bases, though the same in all generic properties with those formed by other acids, are not of similar constitution, and are not even of a saline nature. It unites the advantages, therefore, of both doctrines, and connects under one system facts which are otherwise insulated, and partial generalisations, which, instead of having any relation, seem opposed to each other.

The same general view, I have still to add, may be farther extended. Alkalinity, as well as acidity, is the result apparently of the action of oxygen; the fixed alkalis, the earths, and the metallic oxides, which all contain it as a common element, forming a series in which it is difficult to draw any well-defined line of distinction. Ammonia alone remains an exception: it contains no oxygen, and yet possesses in a very marked degree all the alkaline properties,—an anomaly so great, as to have led almost every chemist to infer that oxygen must exist as an element in one or other of its constituent principles; and as nitrogen is the one apparently least elementary, it has been supposed to be a compound containing oxygen. The result may be accounted for, however, on a very different principle. As hydrogen, in some cases, gives rise, as well as oxygen does, to acidity, so it may in other cases give rise to alkalinity. Under this point of view, ammonia is a compound of which nitrogen is the base, deriving its alkaline power from hydrogen; it stands, therefore, in the same relation to the other alkalis, that sulphuretted hydrogen does to the acids. And thus the whole speculation with regard to the imaginary metallic base Ammonium, and the existence of oxygen in ammonia and in nitrogen, falls to the ground, while the anomaly presented by this alkali is removed.

The fixed alkalis, and the alkaline earths, are considered as containing water in intimate combination, in a definite proportion; and it is doubtful if they can be obtained free from it in an insulated state, retaining at the same time their alkaline properties. It is obvious, however, that the elements of water may exist in combination with the base: that potash, for ex-

ample, is not a compound of an oxide of potassium with water, but of potassium, oxygen and hydrogen. Hence when, on adding water to peroxide of potassium, potash is produced and oxygen gas is disengaged ; this is not owing, as has been supposed, to the excess of oxygen in the peroxide being expelled, and the water taking its place ; but to the water being decomposed, and a portion of its hydrogen entering into the combination, to form the alkali, while the corresponding oxygen is liberated. If hydrogen were brought to act on peroxide of potassium, the alkali would in like manner be formed. With the peroxide of barium, this very change, from the action of hydrogen, takes place ; the hydrogen, according to the usual explanation, combining with its oxygen, and forming water, which unites with the real earth, forming the hydrate ;—in other words, and according to the strict expression of the fact, the hydrogen entering into the composition, and forming the barytes ;—a result perfectly analogous to the formation of muriatic acid from oxymuriatic gas by the agency of hydrogen.

The evidence in support of this doctrine, it is evident, is of the same kind as that with regard to the doctrine applied to the acids. There is the same superior probability in favour of the conclusion, that the elements of water, rather than water itself, exist in these compounds, from the consideration, that modifications of properties so important are more likely to arise from the agency of these elements, than from any action which water can exert. And that water does not exist in them, in consequence of the strength of attraction which the real alkali, as it has been considered, exerts towards it, is evident from this, that on the same principle ammonia ought to contain combined water in its insulated form, which is not the case. The combination of water, therefore, or rather of its principles, in these compounds, depends on relations subsisting among the ultimate elements, not on an affinity exerted by the alkali itself; and this adds confirmation to the conclusion, that these elements are in ternary union.

Their superior alkaline energy, compared with the common metallic oxides, may obviously arise from the joint action of

the hydrogen and oxygen, in the same manner that the acidity of the ternary, compared with the binary acids, is increased by a similar constitution. Thus the class of alkalis will exhibit the same relations as the class of acids. Some are compounds of a base with oxygen: such are the greater number of the metallic oxides, and several, probably, of the earths. Ammonia is a compound of a base with hydrogen. Potash, soda, barytes, strontites, and probably lime, are compounds of bases with oxygen and hydrogen; and these last, like the analogous order among the acids, possess the highest power. Many of the metallic oxides, however, in the state in which they combine with the greatest facility with the acids, are hydrates,— that is, supposed compounds of the oxide with water, but probably ternary compounds of the metal with oxygen and hydrogen; and their facility of combination may depend on this constitution. The same principle explains the necessity, not otherwise easily accounted for, of the presence of water, to enable some of the earths, as barytes, to combine with acids.

There are two views under which the neutral salts may be considered in the preceding theory. It has been shown, that when water is obtained in the action of a salifiable base, whether alkali, earth, or metallic oxide, there is reason to infer that this water is formed by the hydrogen and part of the oxygen of the acid entering into binary combinations; and when water is obtained from an alkali by the action of an acid, there is the same reason to believe, that it is formed by the combination of the hydrogen of the alkali with a portion of its oxygen. In these cases it may be supposed, that the radical of the acid combines with its remaining oxygen, forming a binary compound, which may still be considered as an acid; and that the radical of the alkali combines with its remaining oxygen, forming a binary compound, which may be regarded as an alkali; and these two compounds may unite with each other, forming the neutral salt. This is conformable nearly to the common doctrine. But there is another point of view under which the subject may also be considered. A ternary combination, into which oxygen and hydrogen enter, gives rise apparently to a

higher state of acidity, and to a greater degree of alkaline ener-
gy than is acquired from a mere binary combination into which
oxygen enters. It is doubtful, therefore, if such binary com-
pounds were formed, if they would constitute either acid or al-
kali. And there is at least no proof of their formation. In all
these cases, while the hydrogen combines with the requisite
proportion of oxygen forming water, the radical of the acid,
and that of the base, may enter into union with the remaining
oxygen, and form a ternary compound. And where hydrogen
is not present, such a combination may be at once established.

It is not easy to determine which of these opinions is just.
The reason above stated, renders the latter, perhaps, more pro-
bable ; and the view which leads to the conclusion, that in the
constitution of the acids and alkalis, the three elements, when
present, are in simultaneous combination, leads also to a simi-
lar conclusion with regard to the constitution of the neutral
salts. If this be adopted, neutralisation is not the saturation
of acid with alkali, and the subversion of the properties of the
one by the opposed action of those of the other ; but is the
change of composition of both, and the quiescence of the ele-
ments, in that proportion in which their affinities are in a state
of equilibrium without any excess. The compounds, therefore,
have little activity ; and energy of action is restored only by
the reproduction of substances, which, by their mutual attrac-
tions, tend to the same state of quiescence.

All these results display more fully the extensive relations
of the two elements, oxygen and hydrogen. They do not act
merely in opposition, as had been imagined, but more fre-
quently in union, producing similar effects. Hydrogen is of
nearly equal importance with oxygen, and the principal details
of chemistry consist in their modified action on inflammable
and metallic bodies.

OBSERVATIONS ON THE RELATION OF THE LAW OF DEFI-
NITE PROPORTIONS IN CHEMICAL COMBINATION, TO
THE CONSTITUTION OF THE ACIDS, ALKALIS, AND
EARTHS.

THE law that every body enters into chemical combination
in a certain equivalent weight to others, and that when it com-
bines in different proportions with another, these proportions
have a simple arithmetical ratio, is perhaps the most important
that has hitherto been discovered in the science of chemistry.
It is now so far established, notwithstanding some difficulties
which attend it, that when a view of the constitution of an ex-
tensive series of chemical compounds is brought forward, dif-
ferent from what had hitherto been proposed, it is incumbent
to shew that it is consistent with the operation of this law;
and if just, this may display relations not before observed, and
may obviate objections which have arisen from a different view.
It is from these considerations that I submit the following ob-
servations on the application of the law of definite proportions
to the theory which I have proposed of the chemical constitu-
tion of the acids, alkalis, and their compounds. It necessarily
leads to considerable modifications of these applications; and
the conclusions which these afford, if I am not deceived, afford
proofs of the truth of the opinion I have advanced, and lay
open some new views. The subject is at the same time so ex-
tensive, as to have relations to nearly all the details of chemis-
try.

In the preceding paper I remarked, that the relations in the
proportions of oxygen and hydrogen forming the supposed
portion of combined water in the acids, will probably be those

of one or both of these elements directly to the radical. It re-
mained to be determined how far this is just.

Sulphur affords the best example for illustration, as its com-
binations with oxygen and hydrogen are capable of being ac-
curately determined.

Sulphur and oxygen are held to combine in two definite pro-
portions, forming sulphurous and sulphuric acids. In the first,
100 parts of sulphur are combined with 100 of oxygen; in
the second, 100 are combined with 150 of oxygen, forming
what is called the real acid, with which are farther combined
56.7 of combined water, the entire compound, constituting the
acid in the highest state of concentration, (1.85 of specific gra-
vity,) in which it can be procured in an insulated form.

This constitution of these compounds appears at first view
in opposition to the law of definite proportions in chemical
combinations; for, according to that law, the higher propor-
tion of an element in combination with another is a simple mul-
tiple of the lower proportion in which it combines with the
same body. And hence, since in the first combination of sul-
phur with oxygen, 100 of the former are combined with 100 of
the latter; in the second, 100 ought to be combined with 200,
while the combination is that of 100 to 150. And in the ato-
mic hypothesis, this involves the absurdity of supposing, that
while, in the first compound, the combination, in conformity
to the common rule, is that of one atom of sulphur with one
atom of oxygen; in the second, it is that of an atom of sul-
phur with an atom and a half of oxygen. To obviate this, it
is supposed that a combination of sulphur with a lower propor-
tion of oxygen exists,—an oxide composed of 100 of sulphur
with 50 of oxygen. The ratio will then be that of 1, 2, 3 of
oxygen in the three compounds to one of sulphur. And in the
atomic system, the first will be held to be that of an atom of
sulphur with an atom of oxygen, the second, that of an atom
with two atoms, and the third, that of one with three. To
this, however, it may be objected, that no such oxide of sul-
phur can be obtained, though, if it were a possible combina-
tion, it ought, from the law of attraction, that the first propor-

tion of an element is retained in union with the greatest force, to be the one most permanent and most easily obtained.

Whether this objection be just or not, the difficulty can be solved without any hypothesis, on the view that the elements of the supposed water exist in the composition of the acid; for the quantity of oxygen in this water is just 50; of course, the entire quantity is the regular proportion 200. And the composition is 100 of sulphur, 200 of oxygen, and 6.7 of hydrogen.

This result favours the conclusion, that the relation of the oxygen in common sulphuric acid is entirely that of this element to sulphur; that it is therefore in immediate combination with the radical; and hence, that water does not exist in the constitution of the acid. And even if the existence of an oxide of sulphur and of what is called real sulphuric acid were admitted, the combinations would be strictly conformable to the law of proportions, being those of one of sulphur to 1, 2, 3, and 4 of oxygen.

The proportion of hydrogen is also determined by its relation to the sulphur, for its quantity is that in which they combine, 6.7 of hydrogen with 100 of sulphur constituting the composition of sulphuretted hydrogen.

It thus appears that the proportions of both elements are determined by their relation to the sulphur as the radical of the acid, and are those which the quantity of sulphur would separately require. This, so far as theory can discover, is not a necessary result. The oxygen and hydrogen might each have required the quantity of sulphur with which they combine,— that is, the existing relations might have been those of sulphur to oxygen, and sulphur to hydrogen in their several proportions. It is otherwise; there is the relation of sulphur to oxygen, and in addition to this of hydrogen to the same sulphur. And thus, since the same quantity of sulphur receives the acidifying influence of both elements, we discover the source of the higher degree of acid power. How water should augment acidity, no principle enables us to conjecture. But how the joint operation of two elements acting on the same quantity of radical which each of them separately is capable of

rendering acid, should augment the effect, is easily perceived.
And even from this consideration alone, there can remain lit-
tle hesitation in admitting the conclusion, that both these ele-
ments act directly on the sulphur.—in other words, that the
three are in simultaneous combination.

As there is no proof of the existence of oxide of sulphur, and
as no such compound as that denominated real sulphuric acid,
composed of 100 of sulphur with 150 of oxygen, can be obtain-
ed insulated, it might be supposed that the hypothesis of such
combinations ought to be excluded ; and that the strict fact
only should be admitted, of the two compounds which con-
stitute sulphurous and sulphuric acids.

There is one ground, however, on which it may be inferred
that a relation of sulphur to oxygen, in the proportion of 100
to 150, exists. When sulphuric acid is acted on by a base
neutralizing it, its hydrogen combines with a portion of its
oxygen forming water. The quantity of oxygen thus abstract-
ed is 50, and, of course, the above proportion remains ; and
this being admitted, the existence of oxide of sulphur, it may
be supposed, must also be assumed to bring the results under
the law of definite proportions. And the combinations of oxy-
gen to sulphur will still be in the ratio of 1, 2, 3, 4.

This conclusion, however, does not follow ; for in cases
where this apparent result happens, the oxygen which is ab-
stracted forming water is replaced by the oxygen of the base,
and makes up the proportion of 200 to 100 of sulphur ; and
the new compound is a ternary combination of these elements
in these proportions with the metallic radical of the base.   A
single example will illustrate this.   50.7 of common sulphuric
acid require for saturation 69.6 of oxide of lead ; the former
is composed of 10 of sulphur with 20 of oxygen, and 0.7 of hy-
drogen, the latter of 64.6 of lead with 5 of oxygen.   The hy-
drogen in their mutual action abstracts 5 of oxygen forming
water, and there remain 20 of oxygen, 10 of sulphur, and 64.6
of lead in combination.   The same result is established in all
other cases, and they afford no evidence, therefore, of the ex-
istence of any such compound as that of real sulphuric acid.

But there is another case which does not admit of the same explanation, and in which the relation of 1 of sulphur to $1\frac{1}{2}$ of oxygen seems to be demonstrated. It is that of the action of sulphurous acid on salifiable bases. Here, as there is no abstraction of oxygen in the formation of water, while there is the addition of the oxygen of the base, the proportion in the combination is that of $1\frac{1}{2}$ to 1 of sulphur. This will be apparent from the same example of oxide of lead. 20 of sulphurous acid composed of 10 of sulphur and 10 of oxygen combine with 69.6 of oxide of lead, composed of 64.6 of lead and 5 of oxygen: supposing a simultaneous combination to be established, the proportions will be 10 of sulphur, 15 of oxygen, and 64.6 of lead; and supposing the two latter to observe a relation to sulphur, the proportion is that of 100 to 150 of oxygen.

It might be maintained that no change of composition in the two binary compounds, the sulphurous acid and oxide of lead, takes place, but that they merely unite; or, at least, that while the sulphur and lead display their peculiar relation to each other, each of them retains its relation to oxygen. But this is inconsistent with the general view which has been given of the state of a neutral compound, and can scarcely be supposed to exist with regard to one case, when the reverse is maintained with regard to others.

At the same time, the relation of 100 of sulphur to 200 of oxygen is fully established in common sulphuric acid. Whether it is necessary to admit that of 100 to 50, except on the atomic hypothesis, is not apparent, but it is not improbable.

The same view may be applied to the illustration of the acids of which Carbon is the radical. I have remarked in the preceding paper, that the vegetable acids are to be regarded, not according to the doctrine of Lavoisier, as composed of a compound radical of carbon and hydrogen acidified by oxygen, but as compounds of a simple base, carbon, acidified by oxygen and hydrogen. On this principle the question occurs, what is their precise composition? The proportions assigned by the analyses hitherto given appear at variance with every

principle, and can be brought under no law, nor any analogy whatever; nor has this been attempted. Part of this may arise from the difficulties of the analysis, but more of it perhaps is to be ascribed to the composition not having been considered under the just point of view;—in more recent investigations, particularly in which only accurate experimental results can be expected, to the idea having been entertained that they contain a portion of combined water in their insulated state, which they yield when combined with a base, and that the composition of the acid is to be determined, abstracted from this water, and as it exists in combinations in which it is supposed to be in what is called its real state. The principle which I have applied to their constitution leads to very different results.

In conformity to the law, which it has been shewn exists with regard to sulphur, it is probable the oxygen and hydrogen will be in the definite proportions which they separately observe to carbon. And from the different proportions in which they combine with this element, a number of compounds may be thus formed.

Carbon, with the first proportion of oxygen, forms an oxide. Hydrogen is an acidifying power. Its addition, therefore, it is not improbable, may give rise to acidity, and its proportion will be determined either by its first or second proportion to carbon, or by both. Carbon, with its second proportion of oxygen, forms a weak acid. The addition of hydrogen to this will no doubt augment acidity, and its proportion will also be determined by its first or second proportion to carbon, or both. Four specific compounds will thus be established, which will be represented by carbonic oxide with a certain proportion of hydrogen, one that which exists in carburetted hydrogen, the other that in supercarburetted hydrogen; and by carbonic acid with similar proportions of hydrogen. Farther, there has appeared reason to infer the existence of a relation in proportion of sulphur to oxygen intermediate between that of sulphurous and sulphuric acid; a similar relation may exist in the case of carbon, intermediate between carbonic oxide and carbonic acid; and with the addition of hydrogen, may give rise

to acidity. Lastly, there is some reason also to suppose the existence of a combination of sulphur with oxygen in a lower proportion than that in sulphurous acid. There may be a similar combination with carbon, which may also, with an additional proportion of hydrogen, produce acidity. It remains to inquire how far the composition of any of the vegetable acids can be brought under these laws.

Carbonic acid is the binary compound of carbon and oxygen. With the addition of hydrogen there is every reason to infer, that as in the case of all the other binary acids containing oxygen, an acid will be formed of increased power. Oxalic acid is the strongest of the vegetable acids ; and the results of its analysis will be found to lead to the conclusion that it is this ternary compound.

Berzelius submitted oxalic acid to experiment by combining it with oxide of lead, drying the oxalate and decomposing it by heat. His object in following this method was to abstract the combined water of the acid, and to operate upon it in what is considered as its real state. He accordingly found, that the acid loses water in entering into this combination ; and he objects to a preceding analysis by Gay-Lussac, in which the oxalic acid had been operated on in the state of oxalate of lime, as in this combination the water of composition is not abstracted. His objection is valid, on the doctrine which has been universally adopted by chemists, of acids containing water essential to their constitution, which is abstracted when they enter into combination with a base, such as oxide of lead, in which water is not retained. And if oxalic acid in passing into this combination lose water, as is the case, then on this idea its constitution ought to be determined from its analysis as it exists in a dry oxalate, exactly as that of sulphuric acid is inferred from its analysis in the state in which it exists in a dry sulphate. The reasoning of Berzelius, therefore, was relatively just ; and on these data his results, though they have been objected to, as they involve difficulties in the atomic hypothesis, are correct. But in conformity to the doctrine I have illustrated, it is evident that the composition of the acid is not thus obtained, and

and that what exists in a dry oxalate, such as oxalate of lead,
is a different combination. The crystallized oxalic acid is what
ought to be submitted to analysis if it contained no water of
crystallization; but as it does contain a portion, this is to be
removed, without abstracting what has been called water es-
sential to the acid. It exists in this state in oxalate of lime;
and hence the results given by Gay-Lussac (if experimentally
correct, and they appear to be singularly so) give its real com-
position. They are accordingly strictly conformable to the
view I have stated of the composition of this acid. The pro-
portions he assigns are 26.56 of carbon, 70.69 of oxygen, and
2.75 of hydrogen *. Now carbonic acid is composed of 27.4
of carbon, and 72.6 of oxygen. The proportion of carbon and
oxygen, therefore, in oxalic acid, is precisely the same; and
the sole difference in composition from carbonic acid is in the
proportion of hydrogen it contains.

The constitution of oxalic acid may likewise be inferred
indirectly from the method of Berzelius: and it will be sa-
tisfactory if a coincidence is thus obtained. The composi-
tion of the real acid, as it is called, existing in oxalate of lead,
is stated by Berzelius at 33.22 of carbon, 66.53 of oxygen, and
0.25 of hydrogen. But to this, to express the true composition
of the acid, are to be added the proportions of oxygen and hy-
drogen expended in the formation of water, in the mutual ac-
tion of the acid and the oxide of lead. The quantity of hydro-
gen is inferred from the quantity of oxygen: and there are
different principles connected with the doctrine, as has been
already illustrated in considering the action of sulphuric acid
on a base, whence the proportion of oxygen may be determi-
ned. Thus, it must be a multiple of that existing in the com-
position of what is called the real acid, or in the composition
of the known definite compounds of carbon and oxygen, or it
is equivalent to the oxygen in the base, this quantity of oxy-
gen being always abstracted in the mutual action in combina-
tion with the requisite proportion of hydrogen. Adopting

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* Recherches Phyico-Chimiques, tom. ii, p. 502.

this last principle as the most direct, 106 parts of real oxalic acid, it appears from Berzelius's analysis, combine with 307.5 of oxide of lead: this quantity of oxide contains 22.06 of oxygen, which is therefore to be added to the composition of the acid, with the proportion of hydrogen equivalent to this, 2.94. Hence this quantity of acid, 125 parts, is composed of carbon 33.22, oxygen 88.59, hydrogen 3.19: or in 100 parts the acid consists of 26.5 of carbon, 71 of oxygen, and 2.5 of hydrogen, proportions almost the same as those assigned by Gay-Lussac, and affording a coincidence on a difficult subject of experimental investigation that does honour to the accuracy of these chemists.

There can thus remain no doubt, that the proportion of carbon to oxygen in oxalic acid is the same as that in carbonic acid. The sole difference between them is in the proportion of hydrogen which the former contains: the one is the binary, the other the corresponding ternary compound, similar to what exists in other acids; and hence also, in conformity to the analogy of these acids, and to the principle which accounts for their acidity, is explained the difference in their acid powers.

The compound existing in a dry oxalate, such as oxalate of lead, ought to contain no hydrogen; for the whole of this element, like the hydrogen of sulphuric acid, must, in the action of the base, be combined with oxygen, and abstracted in the state of water. The small portion of hydrogen, therefore, stated by Berzelius, must be considered as derived from error of experiment; and its presence would be admitted more readily from the idea of some portion of hydrogen being essential to the constitution of the acid, as necessary to form what was regarded as its compound radical. In subsequent experiments, accordingly, Berzelius found reason to infer that the proportion was smaller than he had at first assigned. The minute quantity which he does suppose to exist in real oxalic acid, (less than 1 *per cent.*) he brings forward as a difficulty in the atomic hypothesis. A fraction of an atom, he remarked, cannot be supposed; and therefore the small quantity of hydrogen must be considered as an entire atom. But from the propor-

tions it must be held to be combined with 27 atoms of carbon, and 18 atoms of oxygen, that is, with 45 other atoms,—a combination certainly altogether improbable; and any arrangement that can be conceived scarcely lessens the difficulty. Mr Dalton endeavoured to obviate this, by supposing, that in the analysis of Berzelius the hydrogen is underrated. But the reverse is the case. The solution may now be easily given. In the composition which properly constitutes oxalic acid, the proportion of hydrogen is sufficiently large to present no difficulty. And in what was considered as real oxalic acid existing in the dry oxalates, there is no reason to suppose that hydrogen exists. It is also obvious, that the proportion of oxygen and carbon in a dry oxalate is that constituting carbonic acid; for although in the action of the acid on the base a portion of its oxygen is abstracted with its hydrogen, a corresponding portion of oxygen is added from the base or metallic oxide, and a ternary compound is established.

The proportion of hydrogen indicated in the composition of oxalic acid is not conformable to either of the two proportions of carbon and hydrogen, which constitute the two compounds at present admitted as constituting the only definite compounds of these elements, the carburetted and supercarburetted hydrogen. It is much less even than that in the latter, which contains the lower proportion. Yet there is every reason to conclude, from the law which has been illustrated in reviewing the composition of sulphuric acid, that it must exist in a definite relation to the simple radical of the acid, that is to the carbon, conformable to the other relations which subsist between them. It follows, therefore, either that there is an error of analysis, in consequence of which the proportion of hydrogen is greatly underrated, or that there are other definite proportions in which carbon and hydrogen combine, than those which are at present admitted. The coincidence in the results of the analysis by Gay-Lussac and by Berzelius, in a great measure precludes the former supposition; and indeed an error so great would require to be assumed, as cannot be supposed. The other conclusion therefore follows; it is rendered

more probable by other considerations, which give force to the opinion that hydrogen and carbon enter into more numerous proportions than have been assigned: And it is nearly established by the results of this case itself. Supercarburetted hydrogen is composed of 100 of carbon with 17.5 of hydrogen; carburetted hydrogen of 100 with 35. In oxalic acid, 26.5 of carbon are combined, according to the analysis of Berzelius, with 2.5 of hydrogen, which is in the proportion of 100 to 9.4. Now this deviates little, and not more than what may fairly be referred to inaccuracy in the estimation of the proportions in one or other of the compounds, from the fourth of the highest proportion, that in carburetted hydrogen *; and hence, in conformity to the law usually observed, hydrogen probably combines with carbon in proportions following the ratio of 1, 2, 3, 4; and taking a mean which farther investigation may determine with precision, 100 of carbon may be supposed to combine with 9, 18, 27, and 36 of hydrogen. The proportion in oxalic acid will be conformable to the first of these relations, or half that in supercarburetted hydrogen.

Tartaric acid, which is next in strength to the oxalic, or is even equal or superior to it in acidity, appears to be the same combination with a larger proportion of hydrogen.

Gay-Lussac employed tartrate of lime as the medium to decompose the acid. In this state, while the water of crystallization of the acid is excluded, its composition is not subverted, for there is in the formation of tartrate of lime no abstraction of what is called combined water. The results therefore give the real constitution of the acid. The proportions he assigned are carbon 24.05, oxygen 69.3, hydrogen 6.62. Berzelius operated on tartrate of lead. The proportions he assigns are carbon 35.98, oxygen 60.21, hydrogen 3.807. But in the formation of tartrate of lead by the action of the oxide on the acid, a large quantity of water is formed. This being taken

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* The composition of either of the carburetted hydrogen gases is not so well determined, as to exclude a correction sufficient to establish a perfect coincidence.

into calculation, his results agree perfectly with those of Gay-
Lussac.

The proportion of the carbon to the oxygen, it is evident, is
not much different from that which constitutes carbonic acid,
and the deviation is not greater than may fairly come within
the allowance due to errors, liable to be present in a subject
of analysis so difficult.

The proportion of hydrogen is much larger than that in oxa-
lic acid : it must, however, in conformity to the law which has
been stated as regulating the proportions in ternary acids, bear
a certain relation to the radical of the acid, that is to the car-
bon. And it is interesting to discover that this larger quanti-
ty is precisely the other definite proportion which it has ap-
peared from these illustrations must be inferred to exist in the
combinations of carbon and hydrogen. The two known propor-
tions, those existing in supercarburetted and carburetted hy-
drogen, are 100 of carbon to 18 of hydrogen, and 100 to 36 ;
the other two are those of 9 and 27. The first was found in
oxalic acid, and the other is discovered in tartaric acid, the
proportion in the above analysis of 24.05 to 6.62, being that of
100 to 26.5.

In the remaining vegetable acids the composition is evident-
ly less perfectly determined, partly from the difficulty of pro-
curing them insulated, and partly from the sources of error
which attend the experiment, and which have not been checked
or detected by the application of a just principle. It is there-
fore only from repeated experimental investigation, aided by
such an application, that precision can be expected to be ob-
tained. Still some of these results afford very nigh approxi-
mations to the views I have illustrated.

The proportions I assign are those founded on the analyses
by Berzelius, corrected by the theory I have stated. He com-
bined the acid with oxide of lead, and submitted it to decom-
position in this state; the water of composition he supposed to
be thus abstracted, and the real acid obtained. But the com-
position of the acid is in fact subverted, and the water is form-
ed from the combination of its hydrogen with a portion of its

oxygen.   The quantity of oxygen thus lost is discovered by the quantity of oxide which the acid saturates, being equal, according to the principle already explained, to the quantity of oxygen in the oxide.   The hydrogen lost is the quantity equivalent to this.   And these quantities of oxygen and hydrogen being added to the proportions assigned by Berzelius, give the real composition.   It is farther necessary to remark, that as there has appeared reason to infer the existence of 4 definite proportions of oxygen with sulphur, observing the ratio of 1, 2, 3, 4, and 4 proportions of hydrogen with carbon in the same ratio, so there will be found equal reason to infer the existence of 4 similar proportions of oxygen with carbon, 100 of carbon being combined in the first with 62.5 of oxygen, in the second with 125 constituting carbonic oxide, in the third with 187.5, and in the fourth with 250 constituting carbonic acid.   With these preliminary observations it is sufficient to give the general results *.

Citric acid appears to be carbon with oxygen in the third definite proportion, that between carbonic oxide and carbonic acid ; and its hydrogen is nearly in the first proportion of that element to carbon.

Acetic acid is carbon with oxygen in the second proportion nearly, and with hydrogen in exactly the second proportion, that of 100 to 18.   It is represented therefore by carbonic oxide, with hydrogen in the proportion which constitutes supercarburetted hydrogen.

Gallic acid is carbon with oxygen in none of the four definite proportions, but almost exactly in the mean proportion between the first and second.   Its hydrogen is nearly in the first proportion of that element to carbon.

Succinic acid is carbon with oxygen in the second proportion, that constituting carbonic oxide.   The hydrogen conforms to none of the four proportions, but is the precise mean between the first and second.

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* Under the history of the vegetable acids in the 4th Volume, the precise proportions will be found.

In saccho-lactic acid the relation of the oxygen to the car-
bon is not that of any of the definite proportions, but is nighest
to the third. The hydrogen is that which constitutes super-
carburetted hydrogen.

The analysis of benzoic acid is evidently very doubtful, owing
to the difficulties which attend it from its volatility. It is the
only one in which the proportion of oxygen to carbon is less
even than the lowest of the definite proportions of these ele-
ments. The proportion of hydrogen is almost exactly that of
the first proportion.

If the definite proportions of oxygen and hydrogen to car-
bon be assumed to be more numerous than 4, but still ob-
serving the law of simple multiples, all these results may be
easily brought under the law. The relations suggested by these
researches, and particularly those which prove that proportions
of carbon both to oxygen and to hydrogen exist inferior to the
lowest known proportions of these elements, afford much support
to the conclusion, that their definite combinations are more nu-
merous than the few that have been admitted, either on the
doctrine of equivalents, or on the atomic hypothesis. And on
the latter, the composition of organic compounds may be ac-
counted for with this conclusion, so as to preserve what consti-
tutes its chief excellence,—the principle that one body in a
combination is always in the relation of one atom, and which
is confessedly incapable of being maintained, with the assump-
tion merely of the few definite proportions of the elements that
have hitherto been assigned.

The view indeed that the vegetable acids are compounds of
a simple radical (carbon) acidified by oxygen and hydrogen,
and the law existing in this and other ternary combinations,
that two of the elements observe the requisite relations in pro-
portion to the third as a base, may probably be extended to
all the vegetable, and perhaps even to the more complicated
animal products; and, with the admission of a more extensive
series of definite proportions in the primary elements, may re-
move the necessity of the law advanced by Berzelius, and ap-
parently now admitted by the supporters of the atomic system,

that while in inorganic bodies one of the constituents is always in the state of a single atom, in organic bodies it is not so, but very often the reverse. If this law be excluded, and the reverse established, it will assimilate the constitution of organic to that of inorganic compounds, and must contribute greatly, independent of uniformity and simplicity, to render that of the former, at present so involved in obscurity and discordance, more precise.

The compounds of Nitrogen with oxygen present considerable difficulties ; some of them are not easily obtained insulated; the specific distinctions, therefore, which constitute the series, have been variously represented, and the subject is still imperfectly elucidated. Two of them, however, are determined with sufficient precision, from which we may proceed—those constituting the two oxides, the first, nitrous oxide, being composed of 10 of nitrogen with 5.7 of oxygen; the second, nitric oxide, of 10 of nitrogen with 11.4 of oxygen.

These combinations are conformable to the usual law of definite proportions, the oxygen in the one being to that in the other as 2 to 1. It might be expected, therefore, that in the two succeeding compounds admitted by chemists, nitrous and nitric acids, the same ratio would be observed; that the oxygen in the one would be as 3, and in the other as 4. It appears, however, from experimental evidence, that these are not the proportions.

Nitric acid, the extreme of the series, is the one most capable of being obtained uniform, and the composition of which admits, therefore, of the most exact determination. Even with regard to it there are discordant results ; but from those of greatest accuracy the proportions may be fixed at 10 of nitrogen with 28.5 of oxygen,—a proportion of oxygen which is to the first not the multiple of 4, but 5, and which therefore breaks the uniformity of the series.

The composition thus assigned, however, is that of what is called real nitric acid, free from the portion of combined water supposed to exist in the acid in its insulated state, and abstracted when it passes into its saline combinations. If we exclude

this hypothesis, and consider this water as existing in the acid
in the state of its elements, and the acid, therefore, as a ternary compound of nitrogen, oxygen, and hydrogen, this portion
of oxygen is of course to be admitted into the calculation. But
still this does not obviate the difficulty. The quantity of this
water has been variously estimated. If the estimate by Dr
Wollaston be admitted, that of 0.25, it gives the proportion of
10 of nitrogen and 40 of oxygen, which makes the multiple of
oxygen 7, a result equally distant from the regular progression.

The composition of the intermediate compound, Nitrous
Acid, it has been found still more difficult to determine, principally from the difficulty of obtaining it insulated, and free
from all intermixture of nitric acid and nitric oxide. Different
views have been proposed with regard to it to remove the difficulty. Gay-Lussac, in particular, assumed the existence of
two compounds, pernitrous and nitrous acid, intermediate between nitric oxide and nitric acid, which, from their proportions, afforded the intermediate multiples 3, 4, that of real nitric acid being considered as 5. But Dulong has shewn that
these acids are the same. He has also obtained nitrous acid in
its insulated state ; its composition is 10 of nitrogen with 22.8
of oxygen ; a proportion of oxygen which gives the multiple 4,
so that the series is still incomplete, being that of 1, 2, 4, and
either 5, or 7.

When this acid is acted on by an alkaline base it is decomposed, one part passes to the state of nitric acid, and forms a
nitrate, and the other forms a nitrite. It might be supposed,
therefore, that one portion of it yields oxygen to the other,
and that thus a subnitrous acid is formed, which might afford
the intermediate proportion. Nitric oxide gas, however, is disengaged, so that there is probably no reduction in the degree
of oxygenation. And if there were, it would, conformably to
the principle illustrated under the consideration of sulphuric
acid, be replaced by the oxygen of the base, and form the ternary compound constituting the nitrite, so that the relation of
this element to the nitrogen would be the same. There is
therefore no evidence of the existence of any definite compound intermediate between nitrous acid and nitric oxide, and

the ratio of oxygen in nitrous oxide and these two compounds is that of 1, 2, 4.

The proportion in nitric acid, it has been stated, is that which gives the multiple 5 of oxygen. But this applies to what is called the real acid free from water, and no such compound exists, not even in combination with a base; for, as has been already shewn, when an acid yields water from the action of a base, though there is thus an abstraction of a portion of its oxygen, it receives that of the base, and forms a ternary combination, in which the proportion of oxygen to the radical remains the same.

The real composition, therefore, must be determined in its state of hydro-nitric acid. The quantity of combined water, according to the common expression of the fact, existing in it, has been variously stated; but if the estimate in Dr Wollaston's scale of 0.25 in acid of the specific gravity 1.50 be taken, this gives as the composition 10 of nitrogen, with 40 of oxygen and 1.55 of hydrogen: And this again gives 7 as the multiple of oxygen in the series of compounds,—a result which it is scarcely possible to connect according to the established law with the multiple 4, in the lower compound, nitrous acid.

It is certain, however, independent of this circumstance, that the quantity of water, (or of oxygen and hydrogen equivalent to it,) thus assigned, is not the just proportion, essential to the constitution of the acid; for the specific gravity 1.50 is not the highest at which it can be procured. It is obtained with certainty at 1.55 at 60°, by some chemists it is stated at 1.58, and by Proust even at 1.62. At 1.50, therefore, it must be diluted with a certain portion in addition to the real combined water of the common hypothesis. Dr Wollaston has observed, that to decompose nitrate of potash so as to afford nitric acid, it is necessary to employ as much sulphuric acid as forms bi-sulphate of potash, and hence each portion of potash from which dry nitric acid is separated, will displace the water from two equivalents of sulphuric acid. One of these portions of water, it may be presumed then, will go as essential to the constitution of the nitric acid, or rather its oxygen and hy-

drogen will do so, the other is adventitious, though from the volatility and facility of decomposition of the acid it may not be easily abstracted.

On this view, the composition of the acid will be found to be 100 of nitrogen, 34 of oxygen, and 0.76 of hydrogen, which gives 6 as the multiple of oxygen to the first proportion of that element. The proportion of hydrogen is to the nitrogen as the first or lowest equivalent, that in ammonia being the third, the former being 0.76 to 10, the latter to the same quantity of nitrogen 2.3.

The same view of the composition of hydro-nitric acid may be inferred from the proportion of oxygen and nitrogen in the dry nitrates. In these, as in other analogous cases, the abstraction of oxygen in the formation of water at their formation is compensated by the oxygen of the base; the metallic radical of the latter merely replaces the hydrogen of the acid, and the proportion of oxygen to the radical of the acid remains the same.

It thus appears, that the series of the nitrous compounds is nitrous oxide, nitric oxide, nitrous acid, and nitric acid. The oxygen in the first is to the nitrogen as 5.7 to 10; and taking this first proportion of oxygen as 1, that in nitric oxide is 2, in nitrous acid 4, and in hydro-nitric acid 6,—a ratio sufficiently conformable to the law of definite proportions.

If it were admitted, that the oxygen and nitrogen remaining after the action of hydro-nitric acid, and anhydrous nitrous acid, formed binary compounds which entered into direct combination with the alkali, then from the abstraction of one proportion of oxygen in the one by the formation of water, and in the other by the production of nitric acid, compounds would be formed, intermediate in the former between hydro-nitric and nitrous acid, and in the latter between nitrous acid and nitric oxide, and thus the series of the proportions of oxygen of 1, 2, 3, 4, 5, 6, would be completed. This view, however, is not probable. At the same time, the relation of these elements in these intermediate proportions may exist in other ternary compounds, though they are not found in binary combination,

or in the ternary combinations which they form with hydrogen, or with metallic bases.

The composition of the acids, of which Phosphorus is the base, is so imperfectly determined, and the most recent experimental researches are so much at variance in their results, that scarcely any satisfactory application of a principle can be applied to them. There is some reason to believe, that the three acids which appear to be of definite composition, the hypo-phosphorous, phosphorous, and phosphoric acid, contain oxygen in proportions affording the multiples 1, 2, 4. The intermediate multiple of 3 is probably to be found in the combination which is established of phosphorous acid acting on a base, conformable to the view illustrated in the analogous case of sulphurous acid,—the acid receiving the oxygen of the base, and a ternary compound being formed, in which the whole oxygen and the radical of the base observe the due relation to the radical of the acid. And from the quantity of base which phosphorous acid must saturate, this additional proportion of oxygen will be precisely a multiple of that with which phosphorus combines. Phosphoric acid appears to be formed in the combustion of phosphorus in oxygen, and must therefore be admitted to exist as an insulated binary compound. It is farther capable, however, of combining, according to the common expression of the result, with a definite proportion of water, that is, with an additional proportion of oxygen, and with hydrogen equivalent to that proportion. The quantity of this has been variously estimated, and does not appear to be very accurately determined ; but it will probably be equal to an additional multiple of oxygen, that is about 14 in 100, and then the series of phosphoric compounds will contain oxygen in the ratio of 1, 2, 3, 4, 5. If the estimate, however, by Berthollet and Berthier were correct, which makes the quantity of combined water equal to 25 in 100, it would be equal to 2 multiples ; and the series might be 1, 2, 3, 4, 6. And if phosphorous acid does not combine directly with the elements of the alkaline bases, but forms, as has been affirmed, partly phos-

phates, partly phosphites, the series will be that of 1, 2, 4, 6,
similar to that of the nitrous compounds.

In the Muriatic compounds, no regular progression has been
discovered, considering either muriatic acid, or chlorine, as the
first of the series. Some such progression may perhaps, how-
ever, be traced.

Considering muriatic acid as a compound of a radical with
oxygen, Berzelius has inferred, from the application of the
principle, that the quantity of oxygen in an acid is either
equal to, or a simple multiple of the quantity of oxygen in a
base which it saturates, that it consists of 41.632 of radical,
and 58.368 of oxygen. This applies, however, to what is call-
ed the real acid free from water, a compound, the existence
of which is not proved. Taking the proportion of water, or
rather of its elements in hydro-muriatic acid into calculation,
it gives as the composition 31.224 of radical, 65.851 of oxy-
gen, and 2.925 of hydrogen. The proportion of oxygen to
the radical in oxymuriatic acid is the same, the only difference
between the two being the presence of hydrogen in muria-
tic acid ; in oxymuriatic acid, therefore, the proportion is
32.164 of radical, with 67.836 of oxygen. The next com-
pound is Euchlorine, composed of 100 of oxymuriatic acid,
with 22.26 of oxygen ; this is almost exactly the third of the
former ; the relation is, therefore, that of 3, 4. Another gas,
which has since been discovered by Sir H. Davy, contains a
much higher proportion of oxygen, being composed of 100 of
oxymuriatic acid with 89 ; this is exactly 4 multiples, and
gives therefore the series of 3, 4, 7. Hyper-oxymuriatic, or
chloric acid, is composed of 100 of oxymuriatic acid with 111
of oxygen, which is another multiple, or 8. It cannot, how-
ever, exist insulated, as Gay-Lussac states, without the pre-
sence of water, that is, it is a ternary compound, containing
probably an additional multiple of oxygen, and thus affording
the series of 3, 4, 7, 9. If an error of experiment were sup-
posed with regard to the second, or euchlorine, so as to have
deviated from the multiple 5, this would afford a series some-

what regular. But even without assuming this, it is of importance to find in all these, that the proportions are simple multiples of a first quantity. And as the relations of carbon to oxygen and hydrogen, in the composition of the vegetable acids, shew the numerous definite proportions in simple multiples in which they combine, so combinations not more numerous may supply the intermediate multiples in the muriatic compounds.

There is a peculiarity in the muriatic compared with the sulphuric and nitric compounds. In the latter, there does not exist any binary compound of the radical with oxygen, in which the proportion of the one to the other is the same as the proportion in which they exist in the ternary compound which they form with hydrogen. There is therefore no oxysulphuric, or oxynitric acid. In hydromuriatic and oxymuriatic acids, the proportion of oxygen to the radical is the same, and there is only in the former an addition of hydrogen. Hence the apparent peculiarity of oxymuriatic acid having an excess of oxygen, and the circumstance, that by an addition of hydrogen it is converted into muriatic acid. This, however, is not absolutely peculiar to it, and presents therefore no anomaly. The same thing holds in the relation of carbonic and oxalic acids. In both, the same proportion of oxygen to carbon exists; the oxalic acid only containing, like the muriatic acid, an addition, of hydrogen. Did hydrogen act with the same facility on carbonic acid that it does on oxymuriatic acid, it would convert it into oxalic acid in the same manner that it converts the other into muriatic acid. And were the attraction of carbon to metals and inflammables more powerful than it is, so as to bring it into ternary combination with them with oxygen, or its affinity to hydrogen equally strong with that of the radical of muriatic acid, its action, in apparently imparting oxygen, would probably be equally energetic as that of oxymuriatic acid.

The constitution of the Alkalis and Earths, which I have considered as ternary compounds of radicals with oxygen and hydrogen, will be found to exhibit, in conformity to this view, a perfect coincidence with the law of proportions. One or two examples will be sufficient for illustration.

Potassium, in the proportion of 100 with 20.5 of oxygen, constitutes the binary compound denominated dry potash, and which is probably the first degree of oxidation. If, in the ternary compound, which constitutes the alkali in its common state, fused potash as it is named, the additional portion of oxygen is equal to this, or the whole quantity is twice that in the first, conformable to the usual law of proportions, then the quantity of water which will be obtained from the subversion of its composition, and which, according to the common doctrine, is water combined with the alkali, will be 16 from 100 of the fused potash. Now, Berthollet assigned the quantity from experiment at 14, and Sir H. Davy at from 17 to 19. The mean of these may be taken at 16, conformable, therefore, to the theoretical application. And this quantity is stated on the authority of Berzelius as the precise proportion. This second proportion of oxygen seems to be established as an insulated binary compound in combination with the radical, as well as in the ternary combination into which hydrogen also enters, if it is perfectly just, what has been asserted, that the excess of oxygen in the product of the combustion of potassium in oxygen is expelled by heat. And if this compound were capable of being acted on by hydrogen, (which can scarcely be doubted it is,) it would afford another perfect analogy to oxymuriatic acid, as by this action it would be converted into potash, precisely as oxymuriatic acid is by the same action converted into muriatic acid. The facility with which hydrogen is admitted into the binary compound, so as to form the ternary combination, is still greater than the facility with which a similar change is produced in oxymuriatic acid, the addition

of water alone producing the effect, converting the peroxide of potassium into potash, and liberating of course the corresponding excess of oxygen.

Sodium combines with a larger quantity of oxygen than potassium does; and, therefore, soda ought (adopting the language of the common doctrine) to contain a larger quantity of combined water,—the water being always proportional to a multiple of the oxygen combined with the radical. The fact is accordingly conformable to this, 100 of fused soda affording about 24 of water.

Barium, on the contrary, combines with less oxygen. Sir H. Davy, from indirect results, infers, that 89.7 of barium combine with 10.3 of oxygen. In conformity to the law, therefore, barytes ought to afford less water, which is accordingly the case, 100 of hydrate of barytes, as it is named, affording, according to the estimate of Berthollet, 9 of water, according to that of Berzelius about 10.5.

The neutralization of acids and of oxides, by their mutual action, I have already stated, is probably not merely the result of combination, but of subversion of composition. The radical of the acid, and the radical of the base, are in combination with the oxygen which remains after the abstraction of any portion of this element by the formation of water. And the proportions established will be found directly conformable to the relations of these elements. It has been already shewn, (page 657.) that the relation of the oxygen in the ternary combination is that which it separately observes to the radical of the acid, and the relation of the radical of the alkaline base is that which it also separately observes to the radical of the acid. And the three elements exist in simultaneous combination. So far the constitution is analogous to the composition of the ternary acids and bases, with this difference, that in these the oxygen and hydrogen are in their respective proportions to the radical of the acid or base, and in the salts the oxygen and the radical of the base are in their due proportions to the radical of the acid. In the conversion of the one into the other, there is merely the substitution of the radical of the base for the hy-

drogen of the acid, and the abstraction of that portion of oxy-
gen with which the former was combined, and the formation
of a portion of water equivalent to this. In the formation of
a neutral salt from the union of a binary acid, there is simply
the production of a ternary combination in which the propor-
tion of oxygen to the radical of the acid is increased by that
of the base. And the difference in the salts formed by the bi-
nary and ternary acids of the same radical, is in the quantity
of oxygen being a higher multiple in those of the latter than
in those of the former ; so that the addition or abstraction of
that portion of oxygen converts the one into the other.

There is every reason to infer, that in the ternary acids, and
the ternary alkaline bases, while the due relation of oxygen to
the radical, and of hydrogen to the radical exists, there will be
a similar relation in the hydrogen and oxygen to each other:
These two elements combine only in the proportion of 1 to 7.5.
But there may be other proportions multiples or submultiples
of these, in which they exert mutual actions, though they do
not in conformity to them form binary combinations, and they
may exist under the influence of such actions in ternary com-
binations. In hydro-sulphuric acid the quantity of oxygen
in relation to the hydrogen present is four times the quan-
tity of oxygen which constitutes the composition of water.
And this may be a relation actually existing, independent of
the others, that is, while the oxygen in the proportion in
which it is present, acts on the sulphur, and the hydrogen acts
on the sulphur, the oxygen and hydrogen likewise act on each
other ; and these actions are in equilibrium constituting the
sulphuric acid. And in all these ternary compounds at least,
the elements may exist in these uniform relations, instead of
any of them being in any case in intermediate proportions. In
like manner, in the compound salts, the two radicals, that of
the acid, and that of the base will observe their due relation in
proportions to each other.

In the neutral salts, then, there exists neither acid nor alka-
li ; and their decomposition is merely the transfer of the radi-
cal of the base in the one to the radical of the acid of the other.

The decomposition, for example, of nitrate of barytes by sulphate of potash, consists in the transfer of barium to sulphur and oxygen, and of potassium to nitrogen and oxygen. The quantities must be equivalent to each other; and hence the law of Richter, that the state of neutralization remains *.

In the mutual action of acids and salifiable bases with regard to saturation, the simple rule will be, that in all cases an acid will saturate that quantity of a base, the radical of which is in the equivalent weight to the radical of the acid. And the quantity of oxygen in the salt will be that which constitutes the usual proportion of that element to the radical of the acid.

The capacity of saturation in the different acids and bases, in their reciprocal action, has been proposed as a measure of the force of affinity which they exert, those acids being inferred to have the strongest attractions to the salifiable bases, which in the smallest quantities saturate a given weight of these bases ; and the same rule being applied to the attraction of the bases to the acids. The capacity of saturation, however, depends altogether on a different cause,—on the relations of the more remote elements to each other, and not any direct action of acid and base. A larger quantity of barytes is necessary to saturate a given weight of the different acids than of potash, not because barytes has a weaker action on acids than potash has, but because the combining weight of barium is greater than that of potassium, and it combines, therefore, in larger quantity with the radicals of the acids; and conversely, a larger quantity of sulphuric than of carbonic acid is necessary to saturate a given weight of the different bases, not because its affinity to them is less powerful, but because the combining weight of sulphur is higher than that of carbon.

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* Under these principles, the laws given by Berzelius with regard to the quantity of combined water in acids and in bases, and the proportion which the oxygen in an acid bears to the oxygen of an oxide with which it combines, which some have regarded merely as empirical, and which others have denied, are explained. They follow indeed necessarily from the relations in the combining weights of the elements, when these are considered as in simultaneous combination.

And were the doctrine of the influence of elective affinities, in-
dependent of the operation of external forces on chemical at-
traction, established, barytes would be considered as exerting
a more powerful attraction than potash to sulphuric acid, from
the attraction of barium to sulphur being stronger than that of
potassium to sulphur. From the test, however, of the strength
of attraction to be found in the capacity for saturation, the at-
traction of potassium must be inferred to be superior to that of
barium to sulphur; and the results of double decomposition
of what are called their saline compounds must be ascribed, in
conformity to Berthollet's doctrine, to the influence of the
force of cohesion,—this force acting more powerfully on the
ternary compound of barium, sulphur and oxygen, than on that
of potassium, sulphur and oxygen. These views apply to all
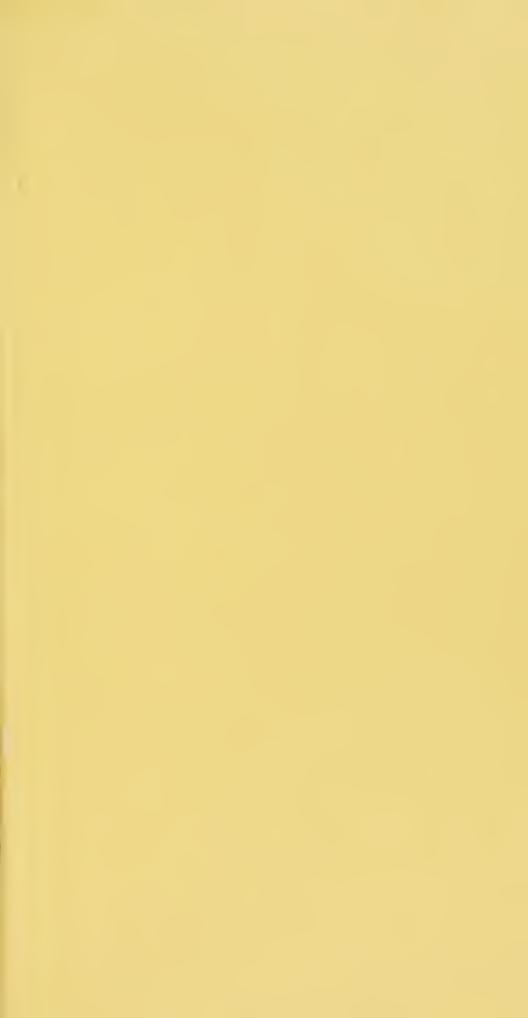the other cases of decomposition in saline combinations.

END OF VOLUME SECOND.